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(54) **A process for synthesizing carboxylate containing modified acrylamide polymers and the polymers thereof.**

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(73) Proprietor: **NALCO CHEMICAL COMPANY**
One Nalco Center
Naperville Illinois 60563-1198(US)

(72) Inventor: **Dodd, Wing Fong**
1275 Leverenz Road
Naperville, Illinois 60565(US)

(74) Representative: **Rotter, Ulrich, Dipl.-Chem. Dr. et al**
Patentanwälte Dipl.-Ing. Olaf Ruschke Dipl.-Ing. Hans E. Ruschke Dipl.-Ing. Jürgen Rost Dipl.-Chem. Dr. U. Rotter Pienzenauerstrasse 2
W-8000 München 80 (DE)

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D scription

This invention relates generally to a process to synthesize water-soluble carboxylated polymers containing various functional groups, and, in addition, which polymers may also contain multiple functional groups which may be useful when applied to aqueous solutions or environments.

Water-soluble polymers are available through various procedures, including condensation polymerization, vinyl polymerization using various free radical catalysts or other catalytic or initiation devices, and even chemical modification of existing polymers by subsequent chemical reaction, such as hydrolysis of pendant amide functional groups to carboxylic acid groups. Chemical modification of existing polymers to achieve water solubility can however lead to other difficulties such as loss of molecular weight and unwanted changes in molecular weight distribution or even cross-linking and possible loss of water solubility. It would therefore be an advance in the art if other water-soluble polymeric chemical structures could be synthesized on a polymeric backbone which structures would contain the carboxylate functional groups, either in the acid or base form, and which structures might also contain multiple and various functional groups which could enhance the use of these water-soluble polymers in certain applications such as dispersants in water treatment, scale inhibitors in natural and industrial waters, flocculants and coagulants, and the like.

It is desired to develop a synthetic procedure which can generally be applicable to the synthesis of various types of water-soluble polymers containing the various functional groups with or without the additional presence of other functional groups which may be useful when these polymers are added to aqueous systems.

Another aim of this invention is to synthesize and recover certain types of carboxylate containing water-soluble polymers which polymers may contain other functional groups such as sulfonate, ether, alkoxyl, ester groups, and/or mixtures thereof, which polymers have not heretofore been known or used.

We have discovered a process for modifying water-soluble polymers containing pendant amide functional groups, such polymers primarily derived from acrylamide containing vinylic polymers/copolymers or from alkyl substituted acrylamide containing vinylic polymers or copolymers, and which polymers/copolymers are water soluble and contain pendant amide functional groups derived from acrylamide, methyl acrylamide, ethylacrylamide.

This process in accordance with the invention uses the equivalent of a transamidation reaction with the pendant amide group on the polymer and a chemical reactant represented by the structure:

Formula I.

$$\overset{\mathrm{R}}{\overset{\vdots}{\mathrm{HN}}}\!-\!(\underset{(\mathrm{X})_m}{\underset{|}{\mathrm{R'}}})\!-\!(\mathrm{COOM})_n$$

wherein

R is individually chosen, in each occurrence, from the group consisting of hydrogen and alkyl groups containing from 1-4 carbon atoms;

M is chosen from the group consisting of hydrogen, alkyl (C_1-C_4) groups, alkali metals, alkaline earth metals, protonated amines, quaternary ammonium and ammonium ions, and mixtures thereof;

R' is a multi-valent hydrocarbonaceous bridging group which may be linear, branched, cyclic, aromatic, heterocyclic, and mixtures thereof, and having from 1-16 carbon atoms;

X is chosen from $-SO_3M$,-OR,

$$-(\mathrm{OCH_2}\overset{\mathrm{R}}{\overset{|}{\mathrm{CH}}})_p\!-\!\mathrm{OR},$$

$-NR''_3$, $-R'NR''_2$, $-PO_3M_2$ $-NR''_4$ and mixtures thereof, and

R'' is chosen from

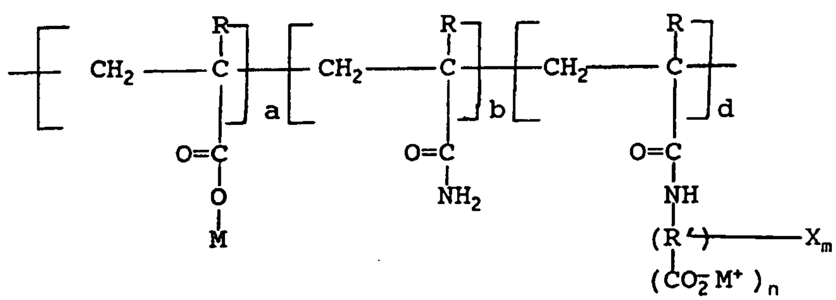
$$(\mathrm{CH_2}\underset{\mathrm{R}}{\underset{|}{\mathrm{C}}}\mathrm{HO})_p\mathrm{R},$$

R and mixtures thereof;
and wherein,

p ranges from 1-16
m ranges between 0 and 16,
n ranges between 1 and 16, provided that the sum of m + n is between 1-20.

In a preferred embodiment the common solvent is water-emulsified in a continuous oil phase such that the water-soluble carboxylated polymer is recovered as a water-in-oil emulsion.

Another aspect of the present invention provides for the synthesis of water-soluble carboxylated polymers represented by the formula:



wherein
R is individually chosen at each occurrence from hydrogen and C_1 to C_4 alkyl, M is individually chosen at each occurrence from hydrogen, alkali metals, tertiary amine salts, and quarternary ammonium and ammonium ions, and mixtures thereof; R' is chosen from multi-covalent, branched alkyl, linear alkyl, alkaryl, aryl or cyclic hydrocarbonaceous bridging groups having from one to eight carbon atoms; X is chosen from $-SO_3H$, OH,

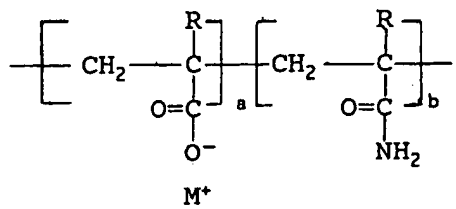
$$-(\mathrm{OCH_2}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}})_p\mathrm{OR},$$

and mixtures thereof;
p ranges from 1 to 12;
m ranges between 0 to 6;
n ranges between 1 to 4;
a, b, and d are integers with the following relationships:

a/b ranges from 0 to 100,
a/d ranges from 0 to 100,
b/d ranges from 0.01 to 100 and
the ratio d:(a + b) is between about 5:1 to about 1:25 and

wherein the occurrence of mer units of a, b and d is random and the sum of a + b + d will achieve a molecular weight of at least 1,000; which process comprises reacting, in an aqueous solvent:

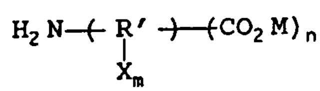
A. a polymer having pendant amide functional groups and represented by the structure:



wherein

R, M, a, and b have the meanings above and wherein the sum of a+b achieves a molecular weight of at least 500; and

B. a reactant having the structure:



wherein R', M, X, m, and n have the meanings above; under the following reaction conditions:

I. a reaction temperature of at least 100 °C;

II. a reaction time of at least 1/4 hour;

III. a mole ratio of chemical reactant to polymer ranging between about 2:1 to about 1:50;

IV. a pressure ranging from atmospheric pressure to 35 times atmospheric pressure;

thereby achieving and thereafter recovering said carboxylated polymers.

In a preferred embodiment the above process provides for a process wherein R is individually chosen at each occurrence from hydrogen or methyl, M is individually chosen at each occurrence from hydrogen, sodium, potassium, ammonium and mixtures thereof, R' is a linear or branched alkylene bridging group having from 2 to 6 carbon atoms;

X is $-SO_3M$,

and mixtures thereof, when p is from 1-8; a, b and d are integers having the following relationships:

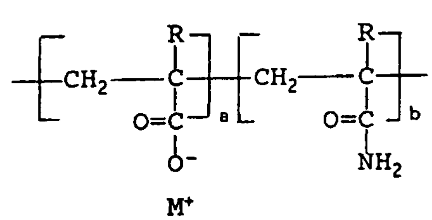
a/b ranges from 0 to 50,

a/d ranges from 0 to 50,

b/d ranges from 0.01 to 10 and

d:(a+b) ranges between about 4:1 and 1:20, and the sum of a+b+d is such that the carboxylated polymer has a molecular weight ranging from 2,000-20,000,000, and which process comprises reacting at a temperature of at least 110 °C for at least 1/2 hour, in a common aqueous solvent,

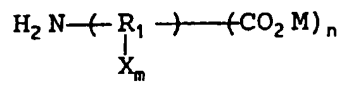
A. a polymer having the structure:



wherein

R, M, a, and b have the meanings above and wherein the sum of a+b is such that the molecular weight of the polymer is at least 2,000; with

B. a chemical reactant having the structure:



wherein

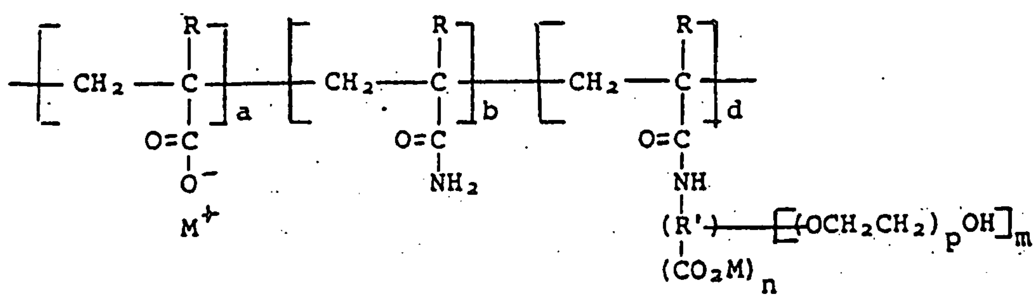
R_1, M, and X are defined above, and

m is from 0 to 3,

n is from 1 to 3, and the sum of m+n is from 1 to 4; and, the ratio of reactant to polymer ranges between about 1:1 to about 1:10, and the reaction pressure is at least 1.25 atmospheres; and then recovering said carboxylated polymer.

In a further preferred embodiment of the previous two processes the aqueous solvent is from the group consisting of water and a water-in-oil emulsion.

Another aspect of the present invention provides for a process for synthesizing a carboxylated polymer represented by:



wherein:

R is individually chosen, at each occurrence, from the group hydrogen, methyl and ethyl groups;

M is individually chosen, at each occurrence, from the group hydrogen, sodium, potassium, tertiary amine salts, and ammonium ions and mixtures thereof;

R' is a linear or branched alkylene bridging group having from 1 to 6 carbon atoms;

p is from 1 to 12;

m is from 1 to 6;

n is from 1 to 6; and the sum, n+m, is from 1-10;

a, b, and d are integers having the relationships:

a/d is from 0 to 50,

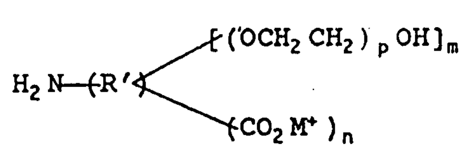
a/b is from 0 to 50,

b/d is from 0.1 to 20,

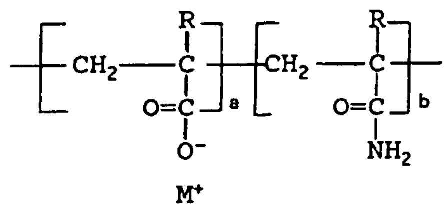
d:(a+b) is from 5:1 to 1:10,

the sum of a+b+d is sufficient to provide a molecular weight of at least 2,000; which process comprises reacting in an aqueous solvent, at a pH between about 3-8, for at least 1/4 hour at a temperature of at least 110°C, in a pressure controlling reactor, the ingredients:

A. a chemical reactant:

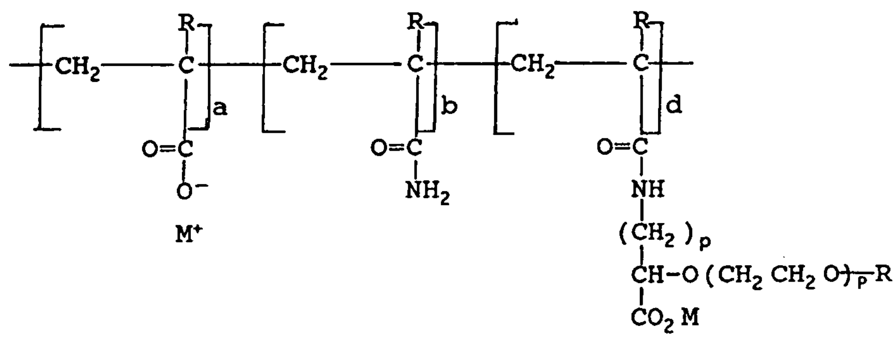


wherein
R', M, p, m and n have the above meanings; and
B. a water-soluble vinyl polymer having pendant amide groups represented by:

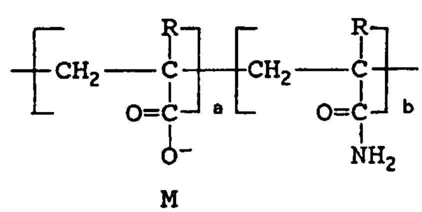


wherein
R, M, a, and b have the above meanings; and
wherein the mole ratio of reactant to pendant amide groups on the polymer ranges between about 1:1 to about 1:5; and then recovering the carboxylated polymer.

Another aspect of the present invention provides for the carboxylated polymer:



which is synthesized, in a pressure controlling reactor, by reacting a precursor polymer:



with a reactant:

$$H_2N\text{—}(CH_2)_p\,\underset{\displaystyle}{\overset{\displaystyle O(CH_2CH_2O)_pR}{\overset{|}{CH}}}\text{—}CO_2M$$

in an aqueous reaction solvent at a temperature of at least 100°C for at least 1/4 hour at a mole ratio of precursor polymer to reactant ranging between about 20:1 to about 1:2, and wherein:

R is chosen individually, at each occurrence, from hydrogen and methyl groups;

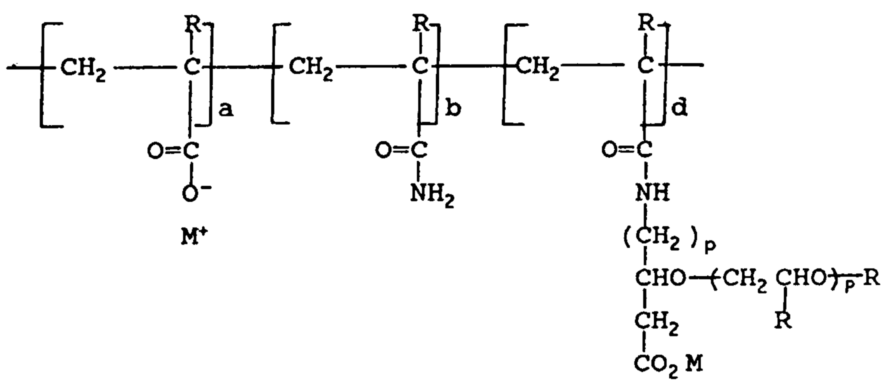
M is chosen individually, at each occurrence, from hydrogen, alkali metal, tertiary amines, and ammonium ions and mixtures thereof;

p ranges, at each occurrence, between 0-12,

a, b, and d are integers having the relationships:
a/d is from 0 to 100,
a/b is from 0 to 100,
b/d is from 0.01 to 100, and
d:(a+b) ranges between about 10:1 to about 1:100, and wherein the sum a+b+d is such that the carboxylated polymer has a molecular weight of at least 1000.

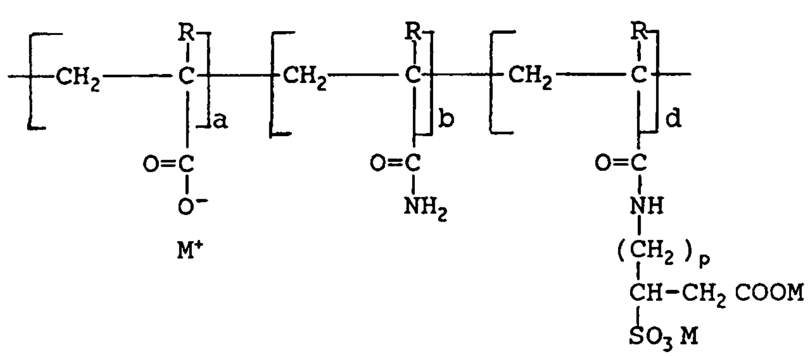
In a preferred embodiment a carboxylated polymer which is synthesized in an aqueous reaction solvent at a temperature of at least 120°C for at least 1 hour at a mole ratio of precursor polymer to reactant of from 10:1 to 1:1 and wherein:
R is hydrogen,
M is from group H, sodium, potassium, and ammonium ions and mixtures thereof, and the polymer has a molecular weight between about 2000 to about 20,000,000.

Another aspect of the present invention provides for a carboxylated polymer represented by the structure:



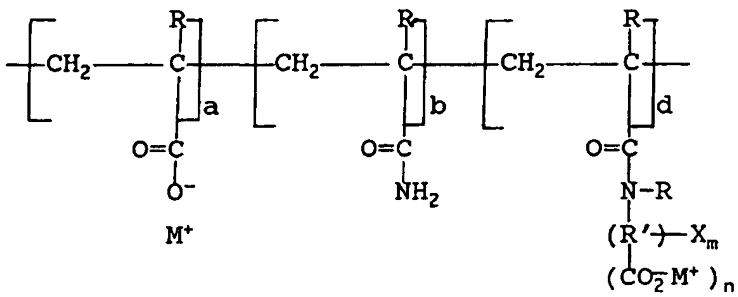
wherein
M is individually chosen, at each occurrence, from hydrogen, sodium, potassium ammonium ions, and mixtures thereof;
a, b, d are integers such that:
the sum of a+b+d is sufficient to achieve a molecular weight of at least 1000;
p, at each occurrence, is from 0-6;
a/d is from 0 to 100;
b/d is from 0.01 to 100;
a/b is from 0 to 100,
and the ratio d:(a+b) ranges between about 5:1 to 1:50.

Another aspect of the present invention provides for a carboxylated polymer represented by:

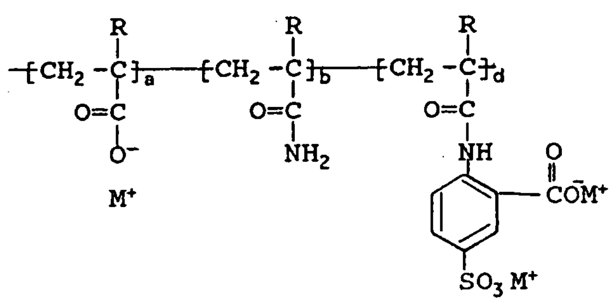


and wherein M, a, b, d and p have the meanings of Claim 11.

Another aspect of the present invention provides for a carboxylated polymer represented by the structure:



wherein
R is individually chosen, at each occurrence, from hydrogen and methyl groups;
M is individually chosen, at each occurrence, from hydrogen, sodium, potassium, and, ammonium ions, and mixtures thereof;
R' is a multivalent hydrocarbonaceous bridging group having from 1-6 carbon atoms and being from linear alkyl, branched alkyl, cyclic, and olefinic groups, and mixtures thereof;
X is $-SO_3M$, OH and mixtures thereof, and wherein a, b, and d are integers, the sum of which is such that the molecular weight of the carboxylated polymer is at least 2,000, and wherein the following relationships exist:
a/b is from 0 to 100,
a/d is from 0 to 100,
b/d is from 0.01 to 1000, and
the ratio d:(a + b) is between about 10:1 to about 1:100, and wherein:
m is equal to 1 to 6,
n is equal to 1 to 6, and the sum of m + n is between 1-8.
The carboxylated polymer represented by the structure:



wherein
R is individually chosen, at each occurrence, from hydrogen and methyl groups;
M is individually chosen at each occurrence, from hydrogen, sodium, potassium, and, ammonium ions, and mixtures thereof; and,
a, b, and d are the same as in claim 13.

THE CHEMICAL REACTANT

The chemical reactant described above is primarily a primary or secondary amino substituted compound which also contains the carboxylate functional group in either the free acid form, an ester form, a salt form, or any combination thereof, and wherein the amine functional group contains at least one active hydrogen substituted on the amino nitrogen. Although carboxylate compounds having both primary and

secondary amines can react under my transamidation reaction conditions to achieve modified carboxylate containing polymers, it is preferable that when a secondary amine is chosen to accomplish this modification of pendant amide containing polymers, that the alkyl group substituted on the amino nitrogen contain no more than 4 carbon atoms, i.e. the alkyl substitution should be limited to methyl, ethyl, propyl and butyl functionality or isomers thereof.

However, it is most preferred that the amine substitution on the carboxylate containing chemical reactant be a primary amino functional group. When a primary amino functional group is used to accomplish the transamidation reaction, the reaction easily proceeds so as to incorporate at least 2, and preferably at least 60, mole percent of the chemical reactant used into the water-soluble polymer chain containing pendant amide groups.

In addition to the amine substitution in the chemical reactant described above, this chemical reactant does contain at least one carboxylate functional group in either its ester form, acid form or its salt form, wherein the salt form is chosen from a salt of an alkali metal, an alkaline earth metal, primary, secondary or tertiary amines, quaternary amines and ammonium ions, and mixtures thereof. The salt form may be in existence prior to the transamidation reaction or it may be synthesized by varying pH with bases containing alkali metals, alkaline earth metals, tertiary amines, quaternary amine bases, or ammonia, either prior to, during the transamidation reaction or after the transamidation reaction has been completed.

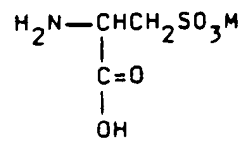
In addition to the carboxylate functional group and the amine functional group, the chemical reactant may also contain other functional groups chosen from the groups consisting of sulfonate, phosphonate, alkoholic, ether, ester, alkoxyl groups, tertiary amino, quaternary amino groups, and mixtures thereof. Preferably, the chemical reactant is limited to contain a primary amino group responsible for the transamidation reaction, at least one carboxylate group which allows the formation of an anionic carboxylate containing water-soluble polymer, and a sulfonate, phosphonate group or an alkoxyl functional group, the presence of which may enhance the activity of water-soluble carboxylate containing polymers synthesized by the process.

Most preferably, the chemical reactant contains a primary amine, one or more carboxyl groups, and one or more carboxylate groups either in the free acid form, salt form, or mixtures of the free acid and salt forms.

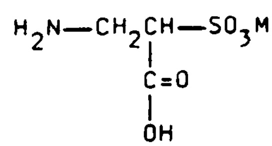
Several preferred species of the chemical reactant described above are demonstrated in the following formulations:

Formula II.

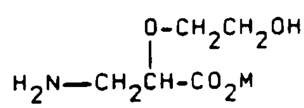
a.



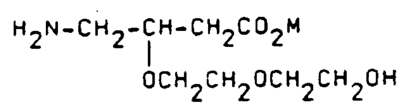
b.



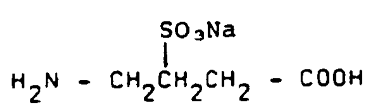
c.



d.



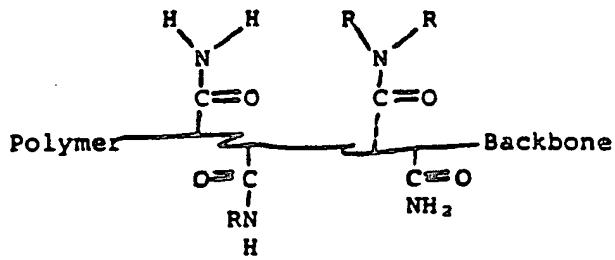
e.



THE PENDANT ACRYLAMIDE CONTAINING POLYMERS

The pendant acrylamide containing polymers are water-soluble polymers which have a general structure allowing the presence of a pendant amide group as demonstrated in Formula III:

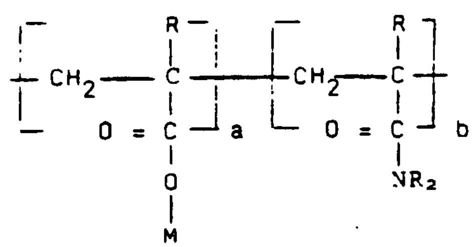
Formula III.



In Formula III, as one can observe, the pendant amide group may be a primary amide, a secondary amide, or a tertiary amide compound or mixtures therof. Preferably, to obtain reasonable conversions of these pendant amide groups to the carboxylate containing functional groups described above, the pendant amide group is a primary amide group.

The most likely water-soluble polymers containing pendant amide functionality which polymers are easily modified under the conditions of the transamidation reaction, are those water-soluble polymers described by Formula IV:

Formula IV.



where the monomer block units of a and b are randomly distributed within the polymer chain.

R is independently chosen, at each occurrence, from the group consisting of hydrogen, and alkyl groups containing from 1-4 carbon atoms;

M is independently chosen, at each occurrence, from hydrogen, alkyl (C_1-C_4) groups, alkali metals, alkaline earth metal and, amine salts, quaternary ammonium ions, ammonium ions and mixtures thereof;

and a and b are integers having the following relationships:

a/b ranges between 0 to 100, and

a + b is sufficient so as to provide a polymer having a molecular weight of at least 500. Preferably the sum,

a + b, is sufficient to provide a molecular weight ranging between about 1,000-20,000,000.

As can be seen, the polymers described above may be homopolymers or copolymers of acrylamide or its alkylated homologs, e.g. methacrylamide, or they may be copolymers of acrylamide and its homologs specifically with acrylic acid or its homologs such as methacrylic acid, or they may be terpolymers and above with other vinylic monomers which terpolymers and above contain acrylamide or its amide homologs with acrylic acid, and their various homologs such as methyacrylic acid, methacylamide, and other additional vinylic monomers such as ethyl acrylate, methylacrylate, ethylene, propylene, vinyl sulfonate.

THE CHEMICAL REACTION

The chemical reaction which is preferred to obtain the carboxylated polymers of this invention is a reaction which can generally be referred to as a transamidation reaction. This reaction substitutes an amine

compound which may also contain other functional groups such as the carboxylate functional group for the nitrogen portion of a pendant amide group contained on a polymeric backbone as described above. This transamidation reaction has been discovered to be a general reaction which can achieve the substitution of an amine and carboxylate containing reactant moiety for the amide nitrogen group of the pendant amide functionality of a water-soluble polymer, thereby obtaining unique carboxylated polymers.

The reaction conditions require that polymers containing pendant amide groups be dissolved or readily dispersed in a solvent which is a common solvent for the chemical reactant of the class described above. In other words, both the polymer which is to be modified and the chemical reactant should be soluble or dispersible in the same solvent system.

Common solvents which have been found useful in this reaction include, but are not limited to, water, diglyme, dimethylformamide, dimethylsulfoxide, admixtures thereof, and admixtures of these solvents, either singly or taken together with other miscible solvents such as ethanol, tertiary butanol, glyme.

A preferred solvent which is a common solvent for both the polymer containing pendant amide groups and the chemical reactants above is water, particularly if the polymer containing pendant amide group is initially water-soluble, as in the case of most acrylamide containing vinylic polymers. Another preferred common solvent for the reaction is a water-in-oil emulsion wherein the dispersed water phase contains dissolved therein both the polymers containing pendant amide groups and the chemical reactants described above.

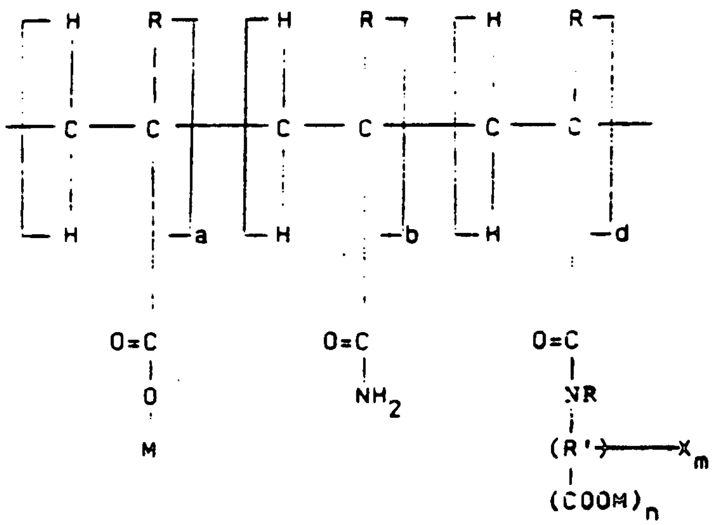
After having dissolved the polymers containing pendant amide groups in the common solvent, preferably water, the chemical reactant can be added to obtain a solution or dispersion of amide containing polymer and the chemical reactants of this invention. Whether the polymer or the reactant is first added to the common solvent is of no consequence. This admixture is then added to or contained in a reaction vessel capable of withstanding a pressurized chemical reaction, for example, a Paar Bomb type of vessel. The vessel is enclosed and then heated to a temperature of at least 100°C, preferably at least 110°C, and most preferably to a temperature of at least 120°C. If the temperature is increased above 100°C, the vessel contents can expand and the pressure within the vessel can exceed one atmosphere and depending upon the solvent, the carboxylate substituted reactants used and/or the reactants used, can reach up to about 5 to 15 atmospheres, and possibly more. The pressure within the reaction vessel is a non-controlled variable and is controlled only to the extent that the vessel is enclosed, that a reaction temperature of at least 100°C or higher is reached, and the vessel may contain solvents or reactants of more or less volatile nature, which solvents and reactants have vapor pressures of such a nature that pressure vessels are required at temperatures above 100°C.

Once the reaction vessel contents have reached at least 100°C, and preferably 110°C, the reaction is allowed to occur for at least 3 minutes at this temperature, and preferably for whatever length of time is necessary to accomplish a minimum of at least a 2 percent conversion, and preferably at least from 25-60 percent conversion, of the added amount of chemical reactant. The chemical reactant is, of course, converted to a pendant carboxylate containing substituted amide, or the product of the transamidation chemical reaction summarized above.

If the polymer is a homopolymer of acrylamide, methacrylamide, or a copolymer of vinyl amide containing monomers such that no other pendant functional group is present besides amide functional groups, the condition of the reaction is such that at least some degree of amide hydrolysis may also occur in those reactions in which water or a water containing solvent is utilized. In such cases, a carboxylate functional group may also be obtained in addition to the carboxylate modified amide and any unreacted starting amide groups from the starting polymer. This is particularly true at very high pH, so it is advisable to operate the reactions in aqueous common solvents or in water-in-oil emulsion at initial pH of below 9.0, and preferably below 8.0.

The invention relates to the chemical reaction or process that accomplishes the synthesis of water soluble carboxylate polymers with randomly distributed monomer units having the structure:

Formula V..



wherein

M is chosen from hydrogen, a lower alkyl (C_1-C_4) group, alkali metal, alkaline earth metal, primary, secondary or tertiary amine salts, quaternary amines and ammonium ions and mixtures thereof; R' is a multi-covalent hydrocarbonaceous bridging group having from one to sixteen carbon atoms and being chosen from linear, branched, cyclic, aromatic and heterocyclic (functional groups), and mixtures thereof; X is chosen from $-SO_3M$, $-PO_3M_2$, -COOR, -OR, -R'NR"$_2$, $-R'N^{+}R_3Hal$,

$$(\mathrm{OCH_2}\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}})_p\mathrm{OR},$$

and mixtures thereof;
where R" is

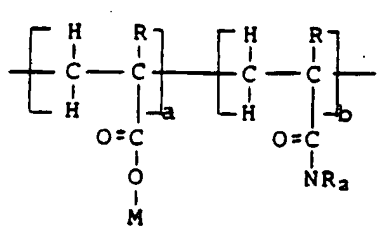
$$(\mathrm{CH_2}\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CHO}})_p\mathrm{R},$$

R, and mixtures thereof;
R is individually chosen at each occurrence from H and lower alkyl (C_1-C_4) groups;

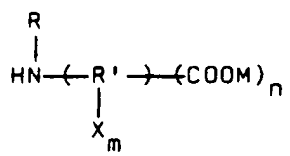
and wherein a, b, and d are integers with the following relationships;
a/b is from zero to 100
b/d is from 0.01 to 100
a/d is from zero to 100,
and the sum of a + b + d is sufficient to provide a molecular weight of at least 1000,
and the ratio of d:(a + b) is from 20:1 to 1:100; and wherein
p ranges between 1 and 16, and
m ranges between 0 and 16, and
n ranges between 1 and 16, provided that when m is zero, the sum of m + n is between 1-20;

which process comprises reacting, in a common solvent at a temperature of at least 100°C:

A. a polymer having a molecular weight of at least 500, and having pendant amide functional groups, which polymer is represented by the structure:



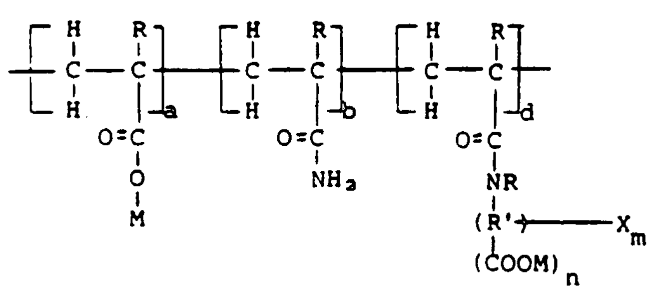
wherein
R, M, a, b have the same meanings as above;
with,
B. a chemical reactant having the structure:



wherein
R, R', M, X, m, and n have the meanings above; wherein the mole ratio of chemical reactant to pendant amide groups ranges between about 5:1 to about 1:100; and the reaction occurs for an effective amount of time to accomplish at least a 2 mole percent, and preferably from 25-60 mole percent conversion of chemical reactant to water-soluble carboxylated polymer; and then recovering the water-soluble carboxylated polymer.

Polymer recovery may be accomplished in several ways known to the person familiar with the art. For example, the polymers may be precipitated by addition of precipitating solvents, or non-solvents, to the reaction mixture. For example, methanol or acetone may be added to the reaction mixture either as is or after concentration by distillation or vacuum distillation to precipitate the polymers. The polymers may also be recovered by vacuum distillation of solvent and unreacted chemical reactant from the reaction product mixture. The polymers may also be recovered by gel permeation chromatographic techniques, however, for the most part the polymers are recovered simply as a solution in the common solvent used to perform the transamidation reaction, and used as such.

Preferably, the process is a method to synthesize water-soluble carboxylated polymers having randomly repeated mer units represented by the formula:



wherein
M is chosen from hydrogen, alkali metal, alkaline earth metal, tertiary amine salts, quaternary amines and ammonium ions and mixtures thereof;
R' is a multi-covalent hydrocarbonaceous bridging group having from one to sixteen carbon atoms and being chosen from linear alkyl, branched alkyl, cyclic, aromatic and heterocyclic (functional groups), and mixtures thereof;
X is chosen from $-SO_3M$, $-PO_3M_2$,

$$-\!\!\left(OCH_2\underset{\displaystyle R}{\underset{|}{C}}H\right)_{\!p}OR,$$

-OR functional groups,

and mixtures thereof;

R is individually chosen at each occurrence from H and alkyl (C_1-C_4) groups;

and wherein . . . .

a, b, and d are integers with the following relationships;

a/b is from zero to 100

b/d is from 0.01 to 100

a/d is from zero to 100,

and the sum of a + b + d is sufficient to provide a molecular weight of at least 3,000,

and the ratio of d:(a + b) is from 20:1 to 1:100;

and wherein

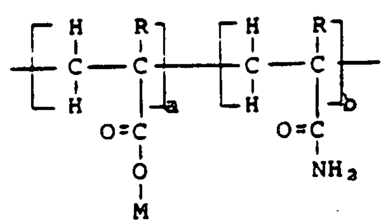
p ranges between 1 and 16, and

m ranges between 0 and 16, and

n ranges between 1 and 16, provided that when m is zero, the sum of m + n is from 1 to 20;

which process comprises reacting, in a common solvent, at a temperature of at least 100°C:

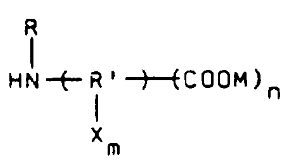
A. a polymer having a molecular weight of at least 500, and having pendant amide functional groups, and represented by the structure:



wherein

R, M, a, b have the same meanings as above; with

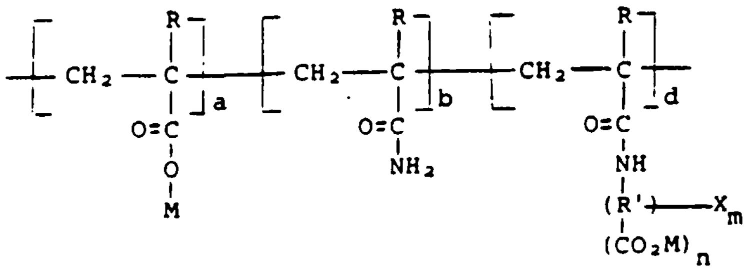
B.a chemical reactant having the structure:



wherein

R, R', M, X, m, and n have the meanings above; and wherein the mole ratio of chemical reactant to pendant amide groups ranges between about 5:1 to about 1:100; and wherein the reaction occurs for an effective amount of time within a pH range of 2-9 in an aqueous solvent to accomplish at least a 50 percent conversion of chemical reactant to water-soluble carboxylated polymer; and then recovering the water-soluble carboxylated polymer.

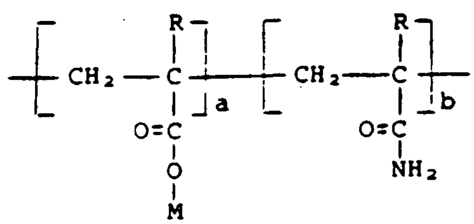
Most preferably, the process is a method for the synthesis of water-soluble carboxylated polymers represented by the formula:



wherein
M is individually chosen at each occurrence from hydrogen, alkali metals, and ammonium ions,
R' is chosen from multi-covalent, branched alkyl, linear alkyl, alkaryl, aryl or cyclic hydrocarbonaceous bridging groups having from one to eight carbon atoms;
X is chosen from $-SO_3M$, OH,

$$-(OCH_2CH_2)_p OR,$$

and mixtures thereof;
p ranges between 1 to 12;
m ranges between 0 to 6;
n ranges between 1 to 4;
R is individually chosen at each occurrence from hydrogen and C_1 to C_4 alkyl groups;
a, b, and d are integers with the following relationships:
a/b ranges from 0 to 100,
a/d ranges from 0 to 100,
b/d ranges from 0.01 to 100, and
the ratio d:(a+b) is between about 5:1 to about 1:25, and
wherein the occurrence of mer units of a, b, and d is random and the sum of a+b+d will achieve a molecular weight of at least 1000; which process comprises reacting, in an aqueous solvent:
A. a polymer having pendant amide functional groups and represented by the structure:



wherein
R, M, a, and b have the meanings above and wherein the sum of a+b achieves a molecular weight of at least 500; and
B. a chemical reactant having the structure:

$$H_2N-(\underset{\displaystyle X_m}{\underset{|}{R'}})-(CO_2M)_n$$

wherein
R', M, X, m, and n have the meanings above;
under the following reaction conditions:
I. a reaction temperature of at least 100 °C and preferably at least 110 °C;

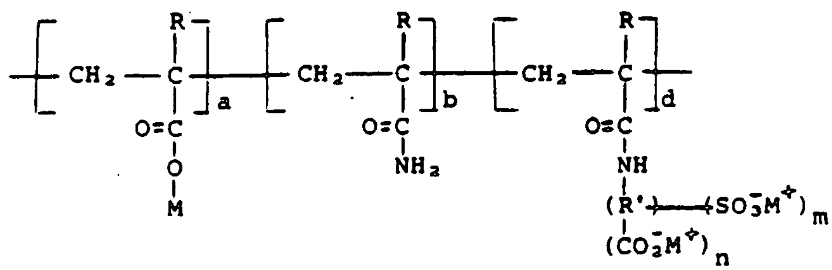
II. a reaction time of at least 1/4 hour and preferably at least 1/2 hour;

III. a mole ratio of chemical reactant to polymer ranging between about 2:1 to about 1:50;

IV. a pressure ranging from atmospheric pressure to 35 times atmospheric pressure, or more;

thereby achieving the synthesis of the carboxylated polymers described above.

It is particularly of interest that the synthetic procedures permit the synthesis of a carboxylated polymer represented by:



wherein:

R is individually chosen, at each occurrence, from the group hydrogen, methyl and ethyl groups;

M is individually chosen, at each occurrence, from the group hydrogen, sodium, potassium, ammonium ions and mixtures thereof;

R' is linear alkylene bridging group having from 1 to 4 carbon atoms;

m is from 0 to 3;

n is from 1 to 3; and

a, b, and d are integers having the relationships:

a/d is from 0 to 50,

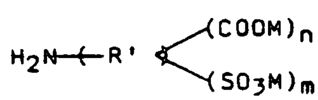
a/b is from 0 to 50,

b/d is from 0.0 to 20,

d:(a + b) is from 5:1 to 1:10,

the sum of a + b + d is sufficient to provide a molecular weight of at least 3,000; which process comprises the reaction, in an aqueous solvent, for at least 1/4 hour at a temperature of at least 110°C, in a pressure controlling reactor, of the ingredients:

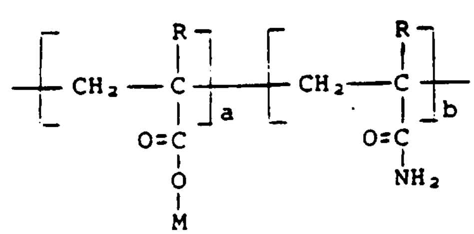
A. a reactant:



wherein

R', M, m and n have the above meanings; and

B. a water-soluble vinyl polymer having pendant amide groups represented by:



wherein

R, M, a, and b have the above meanings; and wherein the mole ratio of reactant to pendant amide

groups ranges between about 1:1 to about 1:5;
and then recovering the carboxylated polymer.

To further illustrate the invention, the following examples are provided. An appropriate procedure would be:

The compositions of the starting polymers vary from homopolyacrylamide to 50 mole percent acrylamide and acrylic acid copolymers. Terpolymer may be used as well as long as acrylamide or its homologs are incorporated therein. The polymers and reactants were charged as aqueous solutions or dispersions to a Paar Bomb equipped with temperature and pressure measuring devices and also equipped with means to agitate the contents. Temperatures were increased to at least 100°C in each case. Reaction times ranged from about 20 minutes to in excess of 4 hours to accomplish the synthesis of the polymers which are described in Table I.

TABLE I

MODIFICATION OF AMIDE-CONTAINING POLYMERS IN WATER

Polymer	Amine (Mole % Changed)	Reaction Temperature	Reaction Time	Recovered Polymer
70 mole % Acrylic Acid/ 30 mole % Acrylamide	Glycine (25)	150°C	4 Hours	85 mole % acrylic acid/ /5 mole % acrylamide/ 10 mole % carboxymethyl-acrylamide
25 mole % Acrylic Acid/ 75 mole % Acrylamide	Aminocaproic Acid (20)	150°C	5 Hours	50 mole % acrylic acid/ 35 mole % acrylamide/ 15 mole % carboxypentyl-acrylamide
25 mole % Acrylic Acid/ 75 mole % Acrylamide	Aspartic Acid (20)	150°C	4 Hours	Acrylic acid/acrylamide 12 mole % N-(1,2-dicarboxy) ethyl-acrylamide
25 mole % Acrylic Acid/ 75 mole % Acrylamide	1-Amino-1-Cyclohexane Carboxylic Acid (20)	150°C	3 Hours	Acrylic acid/acrylamide 15 mole % carboxycyclo-hexylacrylamide
25 mole % Acrylic Acid/ 75 mole % Acrylamide	4-Aminobenzoic Acid (20)	150°C	2 Hours	Acrylic acid/acrylamide 3 mole % carboxyphenyl-acrylamide

In addition, the following polymers would be expected to by synthesized if acrylamide containing polymers were reacted according to the procedure described above with the following chemical reactants, which are described with the anticipated products in Table II.

TABLE II

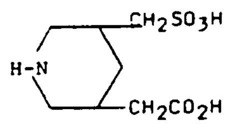
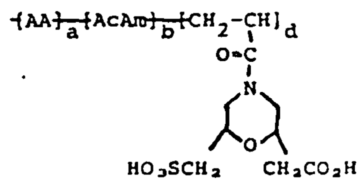
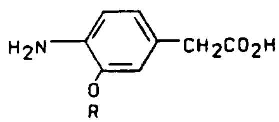
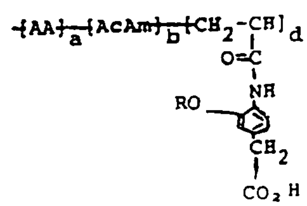
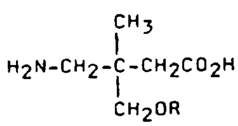
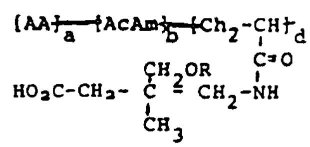
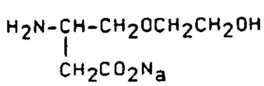
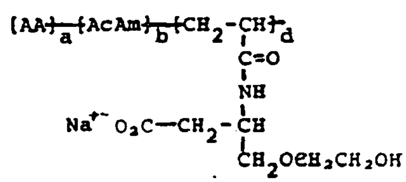
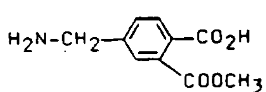
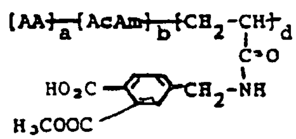
Starting Polymer	Starting Chemical Reactant	Anticipated Product Polymer
$[AA]_a-[AcAm]_b$		
$-[AcAm]_b$	 $R=C_2H_5$	
$[AcAm]_b$	 where R is $-CH_3$	
$[AcAm]_b$		
$-[AcAm]_b$		

TABLE II
(Continued)

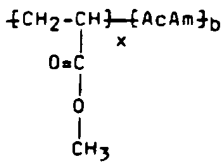
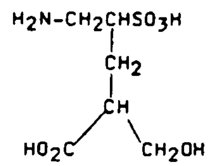
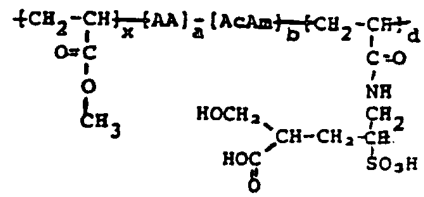
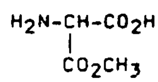
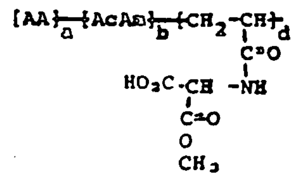
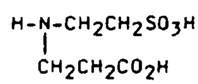
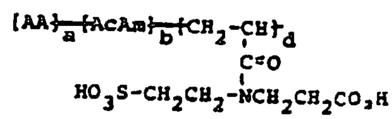
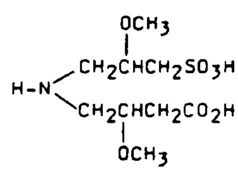
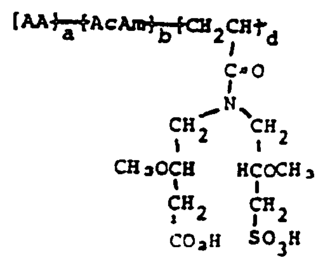
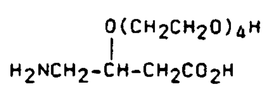
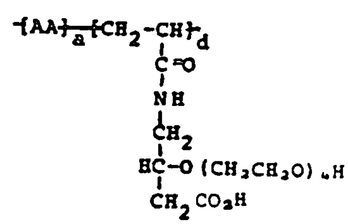
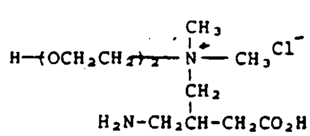
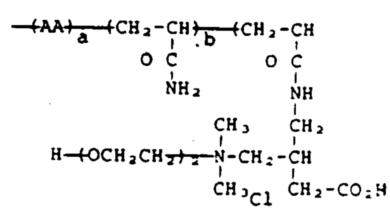
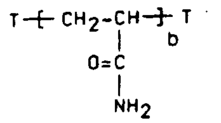
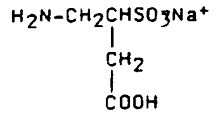
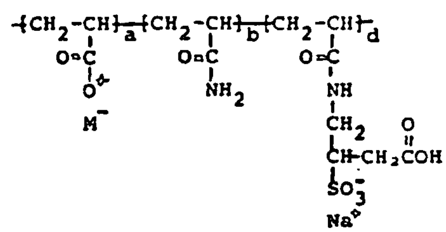
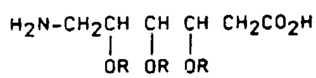
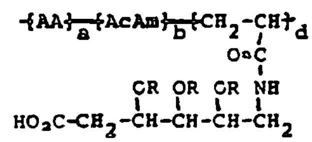
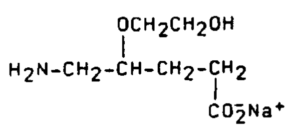
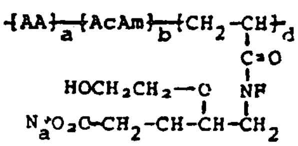
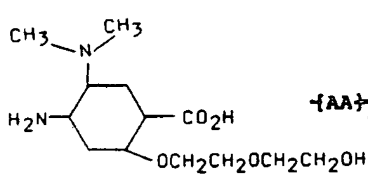
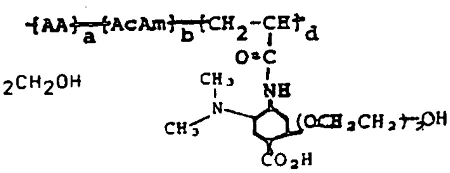
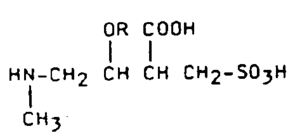
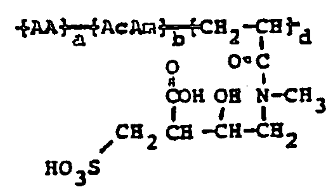
Starting Polymer	Starting Chemical Reactant	Anticipated Product Polymer
		
{AcAm}		
$\{AcAm\}_b$		
$\{AcAm\}_b$		
$\{AA\}_a\{AcAm\}_b$		
$[AcAm]_b$		

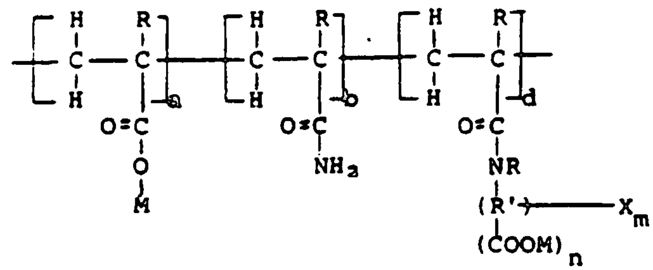
TABLE II
(Continued)

Starting Polymer	Starting Chemical Reactant	Anticipated Product Polymer
 T = any terminal group		
"		
"		
"		
$\{AA\}_a \{AcAm\}_b$		

wherein [AA] = acrylic acid
[AcAm] = acrylamide
a, b, d, R, M, have meanings as described above.

Claims

1. A process to synthesize water-soluble carboxylated polymers having randomly repeated mer units represented by the formula:



wherein
M is chosen from hydrogen, lower alkyl (C_1-C_4) groups, alkali metal, alkaline earth metal, primary, secondary or tertiary amine salts, quaternary amines and ammonium ion, and mixtures thereof;
R' is a multi-covalent hydrocarbonaceous bridging group having from one to sixteen carbon atoms and being chosen from linear alkyl, branched alkyl, cyclic, aromatic, heterocyclic and olefinic groups, and mixtures thereof (functional groups);
X is chosen from $-SO_3M$ - PO_3M_2, $-COOR$, $-OR$, $-R'NR''_2$, $-R'N^+R_3$ Hal

$$(OCH_2\overset{\displaystyle R}{\overset{|}{C}}H)_pOR,$$

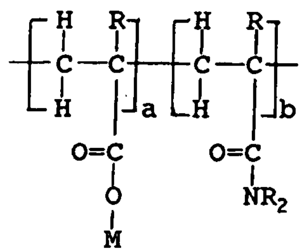
and mixtures thereof;
wherein
R'' is

$$(CH_2\underset{\displaystyle R}{\underset{|}{C}}HO)_pR,$$

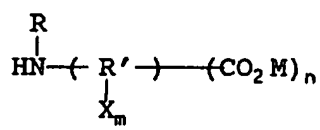
R and mixtures thereof, and
R is individually chosen, at each occurrence, from H and lower alkyl (C_1-C_4) groups;
and wherein

a, b, and d are integers with the following relationships;
a/b is from zero to 100,
b/d is from 0.01 to 100,
a/d is from zero to 100,
and the sum of a+b+d is sufficient to provide a molecular weight of at least 1000,
and the ratio of d:(a+b) is from 20:1 to 1:100; and wherein
p ranges between 1 and 16, and
m ranges between 0 and 16, and
n ranges between 1 and 16, provided that when m is zero, the sum of m+n is from 1 to 20; which process comprises reacting, in a common solvent, at a temperature of at least 100° C;

A. a polymer having a molecular weight of at least 500, and having pendant amide functional groups, and represented by the structure:



wherein
R, M, a, b have the same meanings as above; with
B. a chemical reactant having the structure:



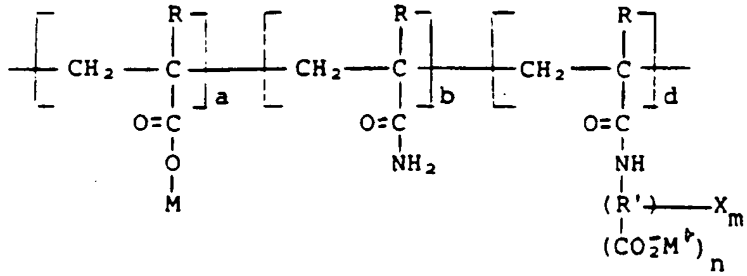
wherein
R, R', M, X, m, and n have the meanings above;
wherein the mole ratio of chemical reactant to pendant amide groups in the polymer ranges between about 5:1 to about 1:100; and reacting for an effective amount of time to accomplish at least a 2 mole percent conversion of chemical reactant to carboxylated pendant groups on the polymer; and then recovering the water-soluble carboxylated polymer.

2. The process of Claim 1 wherein:
R is individually chosen at each occurrence from hydrogen, methyl, and ethyl groups,
M is individually chosen at each occurrence from hydrogen, sodium, potassium, tertiary amines, quaternary ammonium and ammonium ions and mixtures thereof,
R' has from 1-8 carbon atoms and is linear or branched aliphatic, cyclic, aromatic and mixtures thereof;
X is $-SO_3M$, OH, $(OCH_2CH_2)_pOH$; and mixtures thereof
p is from 1 to 12
m is from 0 to 4;
n is from 1 to 4;
and the molecular weight of the water-soluble carboxylated polymer ranges between about 2000 to about 20,000,000.

3. The process of Claim 1 or 2 wherein the common solvent is chosen from the group consisting of water, dimethylformamide, dimethylsulfoxide, diglyme and mixtures thereof.

4. The process of Claim 1 or 2 wherein the common solvent is water-emulsified in a continuous oil phase such that the water-soluble carboxylated polymer is recovered as a water-in-oil emulsion.

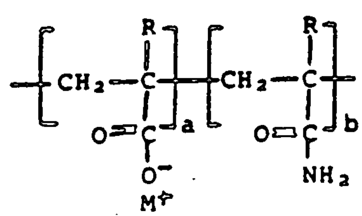
5. The synthesis of water-soluble carboxylated polymers represented by the formula:



wherein
R is individually chosen at each occurrence from hydrogen and C_1 to C_4 lower alkyl,
M is individually chosen at each occurrence from hydrogen, alkali metals, tertiary amine salts, and quarternary ammonium and ammonium ions, and mixtures thereof;
R' is chosen from multi-covalent, branched alkyl, linear alkyl, alkaryl, aryl or cyclic hydrocarbonaceous bridging groups having from one to eight carbon atoms;
X is chosen from $-SO_3H$, OH,

$$-\!\left(OCH_2\underset{\displaystyle R}{\underset{|}{C}}H\right)_{p}\!OR,$$

and mixtures thereof;
p ranges from 1 to 12
m ranges between 0 to 6;
n ranges between 1 to 4;
a, b, and d are integers with the following relationships:
a/b ranges from 0 to 100,
a/d ranges from 0 to 100,
b/d ranges from 0.01 to 100, and
the ratio d:(a + b) is between about 5:1 to about 1:25, and
wherein the occurrence of mer units of a, b, and d is random and the sum of a + b + d will achieve a molecular weight of at least 1,000; which process comprises reacting, in an aqueous solvent:
A. a polymer having pendant amide functional groups and represented by the structure:



wherein
R, M, a, and b have the meanings above and wherein the sum of a + b achieves a molecular weight of at least 500; and
B. a reactant having the structure:

$$H_2N\!-\!\left(\underset{\displaystyle X_m}{\underset{|}{R'}}\right)\!-\!\left(CO_2M\right)_n$$

wherein
R', M, X, m, and n have the meanings above;
under the following reaction conditions:
I. a reaction temperature of at least 100 °C;
II. a reaction time of at least 1/4 hour;
III. a mole ratio of chemical reactant to polymer ranging between about 2:1 to about 1:50;
IV. a pressure ranging from atmospheric pressure to 35 times atmospheric pressure;
thereby achieving and thereafter recovering said carboxylated polymers.

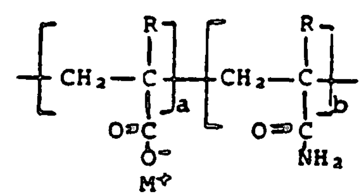
6. The process of Claim 5,
wherein
R is individually chosen at each occurrence from hydrogen or methyl

M is individually chosen at each occurrence from hydrogen, sodium, potassium, ammonium and mixtures thereof,
R' is a linear or branched alkylene bridging group having from 2 to 6 carbon atoms;
X is $-SO_3M$,

$$-O-(CH_2\overset{\displaystyle R}{\overset{|}{C}}HO)_p-R,$$

and mixtures thereof,
when p is from 1-8;
a, b and d are integers having the following relationships:
a/b ranges from 0 to 50,
a/d ranges from 0 to 50,
b/d ranges from 0.01 to 10, and
d:(a+b) ranges between about 4:1 and 1:20,
and the sum of a+b+d is such that the carboxylated polymer has a molecular weight ranging from 2,000-20,000,000, and which process comprises reacting at a temperature of at least 110°C for at least 1/2 hour, in a common aqueous solvent,

A. a polymer having the structure:



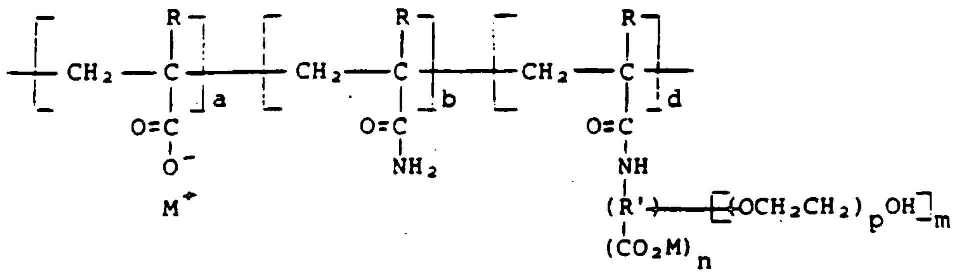
wherein
R, M, a, and b have the meanings above and wherein the sum of a+b is such that the molecular weight of the polymer is at least 2,000; with
B. a chemical reactant having the structure:

$$H_2N-(\underset{\displaystyle X_m}{\underset{|}{R_1}})-(CO_2M)_n$$

wherein
R_1, M, and X are defined above, and
m is from 0 to 3,
n is from 1 to 3, and the sum of m+n is from 1 to 4; and,
the ratio of reactant to polymer ranges between about 1:1 to about 1:10, and the reaction pressure is at least 1.25 atmospheres; and then recovering said carboxylated polymer.

7. The process of Claim 5 or 6 wherein the aqueous solvent is from the group consisting of water and a water-in-oil emulsion.

8. A process for synthesizing a carboxylated polymer represented by:



wherein:

R is individually chosen, at each occurrence, from the group hydrogen, methyl and ethyl groups;

M is individually chosen, at each occurrence, from the group hydrogen, sodium, potassium, tertiary amine salts, and ammonium ions and mixtures thereof;

R' is a linear or branched alkylene bridging group having from 1 to 6 carbon atoms;

p is from 1 to 12;

m is from 1 to 6;

n is from 1 to 6; and the sum, n + m, is from 1-10;

a, b, and d are integers having the relationships:

a/d is from 0 to 50,

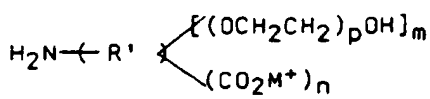
a/b is from 0 to 50,

b/d is from 0.1 to 20,

d:(a + b) is from 5:1 to 1:10,

the sum of a + b + d is sufficient to provide a molecular weight of at least 2,000; which process comprises reacting in an aqueous solvent, at a pH between about 3-8, for at least 1/4 hour at a temperature of at least 110 °C, in a pressure controlling reactor, the ingredients:

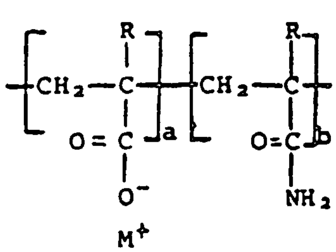
A. a chemical reactant:



wherein

R', M, p, m and n have the above meanings; and

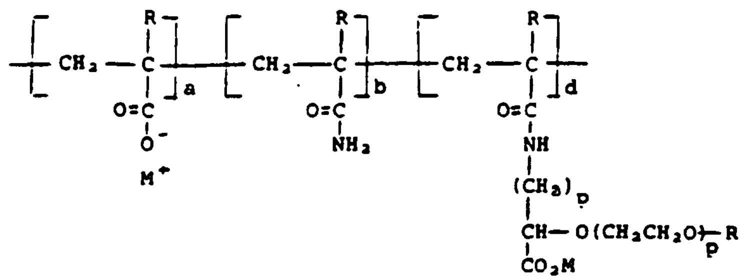
B. a water-soluble vinyl polymer having pendant amide groups represented by:



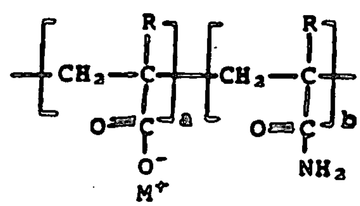
wherein

R, M, a, and b have the above meanings; and wherein the mole ratio of reactant to pendant amide groups on the polymer ranges between about 1:1 to about 1:5; and then recovering the carboxylated polymer.

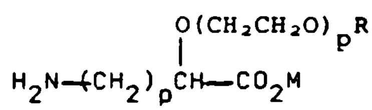
9. The carboxylated polymer:



which is synthesized, in a pressure controlling reactor, by reacting a precursor polymer:



with a reactant:



in an aqueous reaction solvent at a temperature of at least 100°C for at least 1/4 hour at a mole ratio of precursor polymer to reactant ranging between about 20:1 to about 1:2, and wherein:

R is chosen individually, at each occurrence, from hydrogen and methyl groups;

M is chosen individually, at each occurrence, from hydrogen, alkali metal, tertiary amines, and ammonium ions and mixtures thereof;

p ranges, at each occurrence, between 0-12,

a, b, and d are integers having the relationships:

a/d is from 0 to 100,

a/b is from 0 to 100,

b/d is from 0 to 100, and

d:(a + b) ranges between about 10:1 to about 1:100, and wherein the sum a + b + d is such that the carboxylated polymer has a molecular weight of at least 1000.

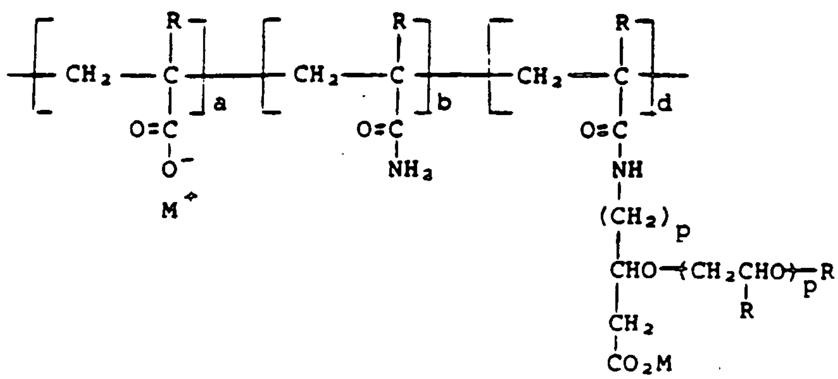
10. The carboxylated polymer of Claim 9 which is synthesized in an aqueous reaction solvent at a temperature of at least 120°C for at least 1 hour at a mole ratio of precursor polymer to reactant of from 10:1 to 1:1 and wherein:

R is hydrogen,

M is from the group H, sodium, potassium, and ammonium ions and mixtures thereof,

and the polymer has a molecular weight between about 2000 to about 20,000,000.

11. The carboxylated polymer represented by the structure:



wherein

M is individually chosen, at each occurrence, from hydrogen, sodium, potassium ammonium ions, and mixtures thereof;

a, b, d are integers such that:

the sum of a + b + d is sufficient to achieve a molecular weight of at least 1000;

p, at each occurrence, is from 0-6;

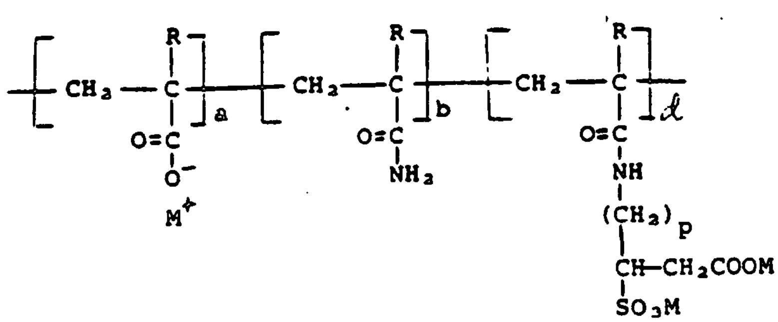
a/d is from 0 to 100;

b/d is from 0.01 to 100;

a/b is from 0 to 100,

and the ratio d:(a + b) ranges between about 5:1 to 1:50.

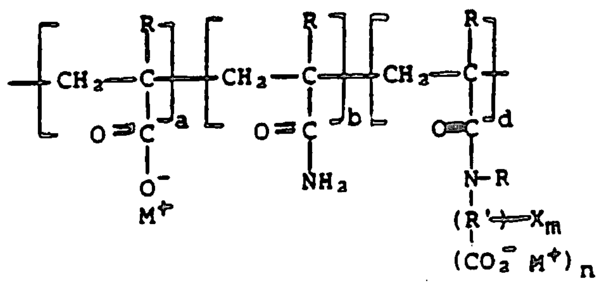
12. The carboxylated polymer represented by:



and wherein

M, a, b, d and p have the meanings of Claim 11.

13. The carboxylated polymer represented by the structure:



wherein

R is individually chosen, at each occurrence, from hydrogen and methyl groups;

M is individually chosen, at each occurrence, from hydrogen, sodium, potassium, and, ammonium ions, and mixtures thereof;

R' is a multivalent hydrocarbonaceous bridging group having from 1 - 6 carbon atoms and being from linear alkyl, branched alkyl, cyclic, and olefinic groups, and mixtures thereof; X is $-SO_3M$, OH and mixtures thereof, and

wherein a, b, and d are integers, the sum of which is such that the molecular weight of the carboxylated polymer is at least 2,000, and wherein the following relationships exist:

a/b is from 0 to 100,

a/d is from 0 to 100,

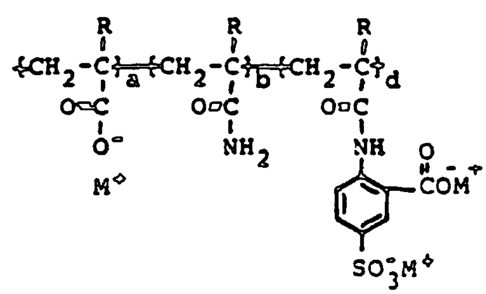
b/d is from 0.01 to 1000, and

the ratio d:(a + b) is between about 10:1 to about 1:100, and wherein:

m is equal to 1 to 6,

n is equal to 1 to 6, and the sum of m+n is between 1-8.

14. The carboxylated polymer represented by the structure:



wherein

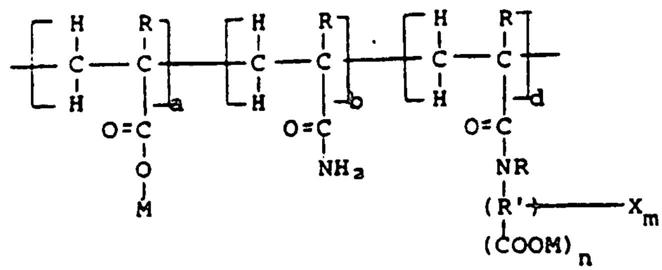
R is individually chosen, at each occurrence, from hydrogen and methyl groups;

M is individually chosen, at each occurrence, from hydrogen, sodium, potassium, and, ammonium ions, and mixtures thereof; and,

a, b, and d are the same as in Claim 13.

Pat ntansprüche

1. Verfahren zum Synthetisieren von wasserlöslichen, Carboxylatgruppen enthaltenden Polymeren mit willkürlich wiederkehrenden Mer-Einheiten, dargestellt durch die Formel



worin:

M ausgewählt wird aus Wasserstoff, niederen (C_1-C_4)-Alkylgruppen, Alkalimetall, Erdalkalimetall, primären, sekundären oder tertiären Aminsalzen, quaternären Aminen und dem Ammoniumion und Mischungen davon;

R' steht für eine multi-kovalente, brückenbildnede Kohlenwasserstoff-Gruppe mit 1 bis 16 Kohlenstoffatomen, die ausgewählt wird aus linearen Alkyl-, verzweigten Alkyl-, cyclischen, aromatischen, heterocyclischen und olefinischen Gruppen und Mischungen davon (funktionelle Gruppen);

X ausgewählt wird aus $-SO_3M$, $-PO_3M_2$, -COOR, -OR, -R'NR"$_2$, $-R'N^+R_3$-Hal,

$$(OCH_2\underset{|}{\overset{R}{C}}H)_pOR,$$

und Mischungen davon, worin R" steht für

$$(CH_2\underset{R}{\overset{|}{C}}HO)_pR,$$

R und Mischungen davon; und

R bei jedem Vorkommen einzeln ausgewählt wird aus H und niederen (C_1-C_4)-Alkylgruppen;

a, b und d stehen für ganze Zahlen mit den folgenden Beziehungen:

a/b = 0 bis 100

b/d = 0,01 bis 100

a/d = 0 bis 100

die Summe a+b+d reicht aus zur Erzielung eines Molekulargewichtes von mindestens 1000 und das Verhältnis d:(a+b) = 20:1 bis 1:100; und

p liegt in dem Bereich zwischen 1 und 16,

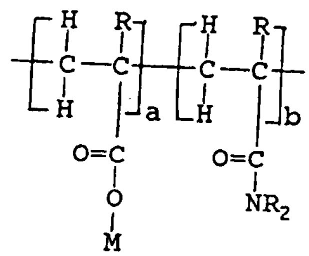
m liegt in dem Bereich zwischen 0 und 16 und

n liegt in dem Bereich zwischen 1 und 16,

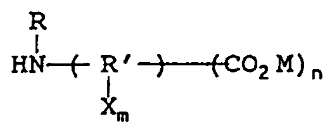
mit der Maßgabe, daß dann, wenn m = 0, die Summe m+n = 1 bis 20,

das umfaßt die Umsetzung, in einem gemeinsamen Lösungsmittel, bei einer Temperatur von mindestens 100 °C zwischen

A) einem Polymer mit einem Molekulargewicht von mindestens 500, das seitenständige (anhängende) funktionelle Amidgruppen aufweist und die Struktur hat:



worin
R, M, a, b die gleichen Bedeutungen wie oben haben; und
B) einem chemischen Reaktanten mit der Struktur



worin
R, R', M, X, m und n die oben angegebenen Bedeutungen haben;
wobei das Molverhältnis zwischen dem chemischen Reaktanten und den seitenständigen (anhängenden) Amidgruppen in dem Polymer in dem Bereich zwischen etwa 5:1 und etwa 1:100 liegt; und
die Durchführung der Reaktion für eine wirksame Zeitspanne zur Erzielung einer mindestens 2 mol-%igen Umwandlung des chemischen Reaktanten in seitenständige Carboxylat-Gruppen an dem Polymer; und
die anschließende Gewinnung (Abtrennung) des wasserlöslichen, Carboxylatgruppen enthaltenden Polymers.

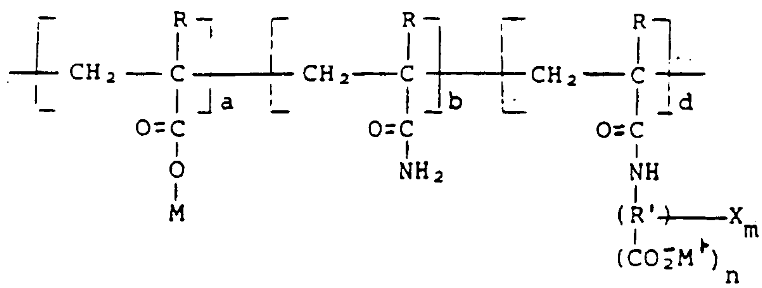
2. Verfahren nach Anspruch 1, worin
   - R bei jedem Vorkommen einzeln ausgewählt wird aus Wasserstoff, Methyl- und Ethylgruppen,
   - M bei jedem Vorkommen einzeln ausgewählt wird aus Wasserstoff, Natrium, Kalium, tertiären Aminen, quaternärem Ammonium und Ammoniumionen und Mischungen davon,
   - R' 1 bis 8 Kohlenstoffatome aufweist und linear oder verzweigt, aliphatisch, cyclisch oder aromatisch ist und Mischungen davon;
   - X steht für $-SO_3M$, OH, $(OCH_2CH_2)_pOH$ und Mischungen davon;
   - p steht für eine Zahl von 1 bis 12;
   - m steht für eine Zahl von 0 bis 4;
   - n steht für eine Zahl von 1 bis 4;

   und wobei das Molekulargewicht des wasserlöslichen, Carboxylatgruppen enthaltenden Polymers in dem Bereich zwischen etwa 2000 und etwa 20 000 000 liegt.

3. Verfahren nach Anspruch 1 oder 2, bei dem das gemeinsame Lösungsmittel ausgewählt wird aus der Gruppe, die besteht aus Wasser, Dimethylformamid, Dimethylsulfoxid, Diglyme und Mischungen davon.

4. Verfahren nach Anspruch 1 oder 2, bei dem das gemeinsame Lösungsmittel Wasser ist, das in einer kontinuierlichen Ölphase emulgiert ist, so daß das wasserlösliche, Carboxylatgruppen enthaltende Polymer in Form einer Wasser-in-Öl-Emulsion gewonnen (abgetrennt) wird.

5. Verfahren zum Synthetisieren von wasserlöslichen Carboxylatgruppen enthaltenden Polymeren der Formel



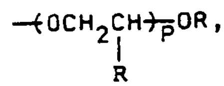
worin:

R bei jedem Vorkommen einzeln ausgewählt wird aus Wasserstoff und niederem C_1-C_4-Alkyl,

M bei jedem Vorkommen einzeln ausgewählt wird aus Wasserstoff, Alkalimetallen, tertiären Aminsalzen und quaternärem Ammonium und Ammoniumionen und Mischungen davon;

R' ausgewählt wird aus multi-kovalenten, brückenbildenden verzweigten Alkyl-, linearen Alkyl-, Alkaryl-, Aryl- oder cyclischen Kohlenwasserstoff-Gruppen mit 1 bis 8 Kohlenstoffatomen;

X ausgewählt wird aus $-SO_3H$, OH,



und Mischungen davon;

p in dem Bereich von 1 bis 12 liegt;

m in dem Bereich von 0 bis 6 liegt;

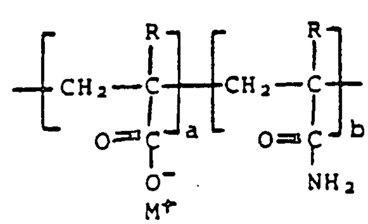
n in dem Bereich von 1 bis 4 liegt;

a, b und d stehen für ganze Zahlen mit den folgenden Beziehungen:
a/b liegt in dem Bereich von 0 bis 100,
a/d liegt in dem Bereich von 0 bis 100,
b/d liegt in dem Bereich von 0,01 bis 100 und
das Verhältnis d:(a + b) liegt zwischen etwa 5:1 und etwa 1:25 und

wobei das Auftreten der Mer-Einheiten von a, b und d willkürlich ist und die Summe a + b + d ausreicht zur Erzielung eines Molekulargewichtes von mindestens 1000;

das umfaßt die Umsetzung in einem wäßrigen Lösungsmittel zwischen

A) einem Polymer mit seitenständigen funktionellen Amid-Gruppen mit der Struktur



worin

R, M, a und b die oben angegebenen Bedeutungen haben und die Summe a + b ausreicht zur Erzielung eines Molekulargewichtes von mindestens 500; und

B) einem Reaktanten mit der Struktur

$$H_2N\text{—}(\underset{\underset{X_m}{|}}{R'})\text{—}(CO_2M)_n$$

worin
R', M, X, m und n die oben angegebenen Bedeutungen haben;
unter den folgenden Reaktionsbedingungen:

I. die Reaktionstemperatur beträgt mindestens 100 °C;
II. die Reaktionszeit beträgt mindestens 1/4 h;
III. das Molverhältnis zwischen dem chemischen Reaktanten und dem Polymer liegt in dem Bereich zwischen etwa 2:1 und etwa 1:50;
IV. der Druck liegt in dem Bereich von Atmosphärendruck bis 35 Atmosphären;

wodurch die Carboxylatgruppen enthaltenden Polymeren gebildet und anschließend gewonnen (abgetrennt) werden.

6. Verfahren nach Anspruch 5, worin:

R	bei jedem Vorkommen einzeln ausgewählt wird aus Wasserstoff oder Methyl,
M	bei jedem Vorkommen einzeln ausgewählt wird aus Wasserstoff, Natrium, Kalium, Ammonium und Mischungen davon;
R'	steht für eine lineare oder verzweigte brückenbildende Alkylen-Gruppe mit 2 bis 6 Kohlenstoffatomen;
X	steht für $-SO_3M$,

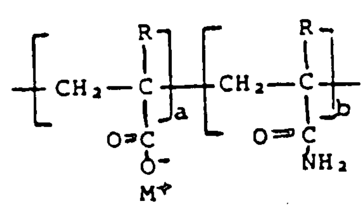
$$-O\text{—}(CH_2\overset{\overset{R}{|}}{C}HO)_p\text{—}R,$$

und Mischungen davon, wenn p = 1 bis 8;

a, b und d stehen für ganze Zahlen mit den folgenden Beziehungen:
a/b liegt in dem Bereich von 0 bis 50,
a/d liegt in dem Bereich von 0 bis 50,
b/d liegt in dem Bereich von 0,01 bis 10 und
d:(a + b) liegt in dem Bereich zwischen etwa 4:1 und 1:20,

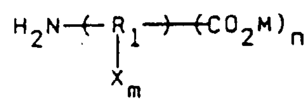
wobei die Summe a + b + d so groß ist, daß das Carboxylgruppen enthaltende Polymer ein Molekulargewicht in dem Bereich von 2000 bis 20 000 000 hat,
das umfaßt die Umsetzung bei einer Temperatur von mindestens 110 °C für mindestens 1/2 h in einem gemeinsamen wäßrigen Lösungsmittel zwischen

A) einem Polymer mit der Struktur



worin
R, M, a und b die oben angegebenen Bedeutungen haben und die Summe a + b so groß ist, daß das Molekulargewicht des Polymers mindestens 2000 beträgt; und

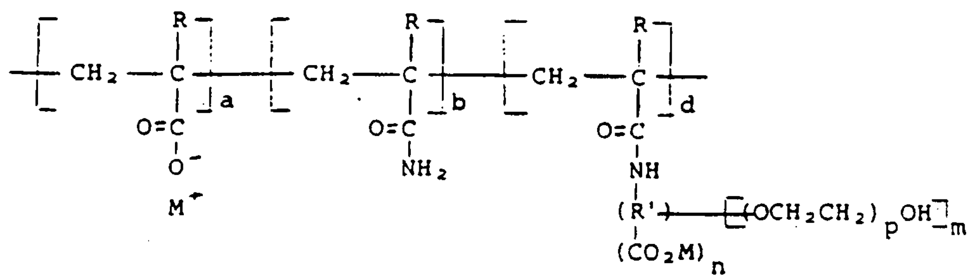
B) einem chemischen Reaktanten mit der Struktur



worin
R_1, M und X wie oben definiert sind und m für 0 bis 3 und n für 1 bis 3 stehen und die Summe m + n 1 bis 4 beträgt; und das Verhältnis zwischen dem Reaktanten und dem Polymer in dem Bereich zwischen etwa 1:1 und etwa 1:10 liegt und der Reaktionsdruck mindestens 1,25 Atmosphären beträgt, und
das anschließende Gewinnen (Abtrennen) des Carboxylatgruppen enthaltenden Polymers.

7. Verfahren nach Anspruch 5 oder 6, bei dem das wäßrige Lösungsmittel ausgewählt wird aus der Gruppe, die besteht aus Wasser und einer Wasser-in-Öl-Emulsion.

8. Verfahren zum Synthetisieren eines Carboxylatgruppen enthaltenden Polymers der Formel

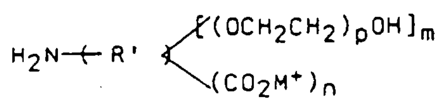


worin:

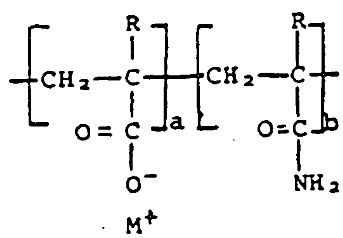
R	bei jedem Vorkommen einzeln ausgewählt wird aus der Gruppe Wasserstoff, Methyl- und Ethylgruppen;
M	bei jedem Vorkommen einzeln ausgewählt wird aus der Gruppe Wasserstoff, Natrium, Kalium, tertiären Aminsalzen und Ammoniumionen und Mischungen davon;;
R'	steht für eine brückenbildende lineare oder verzweigte Alkylengruppe mit 1 bis 6 Kohlenstoffatomen;
p	steht für eine Zahl von 1 bis 12;
m	steht für eine Zahl von 1 bis 6;
n	steht für eine Zahl von 1 bis 6, wobei die Summe n + m steht für eine Zahl von 1 bis 10;
a, b und d	stehen für ganze Zahlen mit den folgenden Beziehungen: a/d = 0 bis 50; a/b = 0 bis 50; b/d = 0,1 bis 20; d:(a + b) = 5:1 bis 1:10

wobei die Summe a + b + d ausreicht zur Erzielung eines Molekulargewichtes von mindestens 2000, das umfaßt die Umsetzung in einem wäßrigen Lösungsmittel bei einem pH-Wert zwischen etwa 3 und 8 für mindestens 1/4 h bei einer Temperatur von mindestens 110 °C in einem Druck-Kontroll-Reaktor zwischen den folgenden Komponenten:

A) einem chemischen Reaktanten der Formel

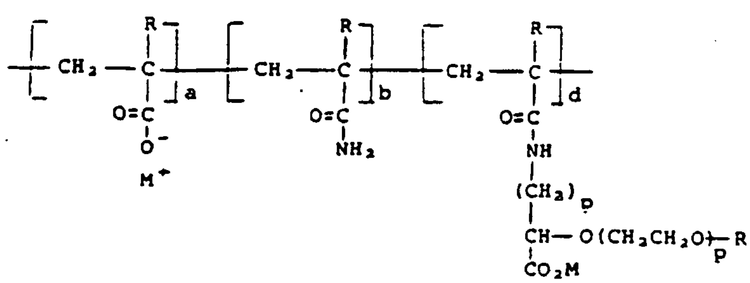


worin
R', M, p, m und n die oben angegebenen Bedeutungen haben; und
B) einem wasserlöslichen Vinylpolymer mit seitenständigen Amidgruppen der Formel

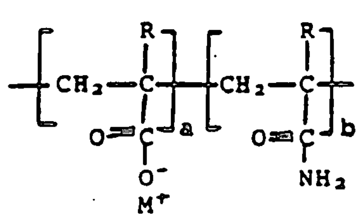


worin
R, M, a und b die oben angegebenen Bedeutungen haben; und
wobei das Molverhältnis zwischen dem Reaktanten und den seitenständigen Amidgruppen an dem Polymer in dem Bereich zwischen etwa 1:1 und etwa 1:5 liegt, und
das anschließende Gewinnen (Abtrennen) des Carboxylatgruppen enthaltenden Polymers.

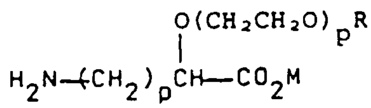
9. Carboxylatgruppen enthaltendes Polymer der Formel



das in einem Druck-Kontroll-Reaktor synthetisiert worden ist durch Umsetzung eines Vorläufer-Polymers der Formel



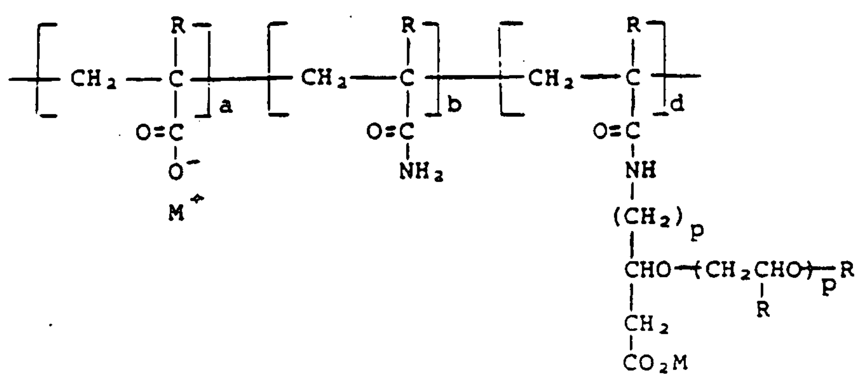
mit einem Reaktanten der Formel



in einem wäßrigen Reaktionslösungsmittel bei einer Temperatur von mindestens 100 °C für mindestens 1/4 h bei einem Molverhältnis von Vorläufer-Polymer zu Reaktant in dem Bereich zwischen etwa 20:1 und etwa 1:2, worin:
R bei jedem Vorkommen einzeln ausgewählt wird aus Wasserstoff und Methylgruppen;
M bei jedem Vorkommen einzeln ausgewählt wird aus Wasserstoff, Alkalimetall, tertiären Aminen und Ammoniumionen und Mischungen davon;
p bei jedem Vorkommen in dem Bereich zwischen 0 bis 12 liegt;
a, b und d stehen für ganze Zahlen mit den folgenden Beziehungen:
a/d = 0 bis 100,
a/b = 0 bis 100
b/d = 0,01 bis 100 und
d:(a + b) liegt in dem Bereich zwischen etwa 10:1 und etwa 1:100,
wobei die Summe a + b + d so groß ist, daß das Carboxylatgruppen enthaltende Polymer ein Molekulargewicht von mindestens 1000 hat.

10. Carboxylatgruppen enthaltendes Polymer nach Anspruch 9, das in einem wäßrigen Reaktionslösungsmittel bei einer Temperatur von mindestens 120 °C für mindestens 1 h bei einem Molverhältnis von Vorläufer-Polymer zu Reaktant von 10:1 bis 1:1 synthetisiert worden ist und worin:
R steht für Wasserstoff,
M steht für die Gruppe H, Natrium, Kalium und Ammoniumionen und Mischungen davon,
wobei das Polymer ein Molekulargewicht zwischen etwa 2000 und etwa 20 000 000 hat.

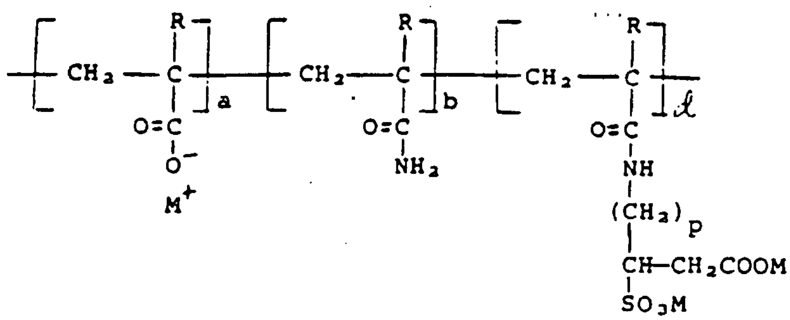
11. Carboxylatgruppen enthaltendes Polymer mit der Struktur



worin

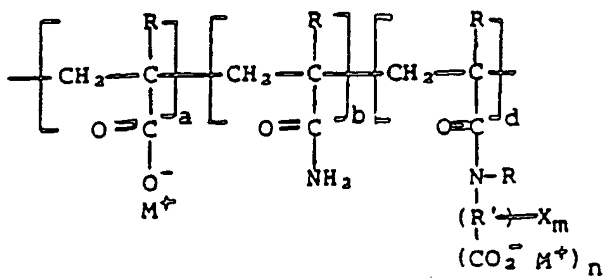
M	bei jedem Vorkommen einzeln ausgewählt wird aus Wasserstoff, Natrium, Kalium, Ammoniumionen und Mischungen davon;
a, b, d	stehen für ganze Zahlen, so daß die Summe a + b + d ausreicht zur Erzielung eines Molekulargewichtes von mindestens 1000;
p	bei jedem Vorkommen steht für 0 bis 6;
	a/d = 0 bis 100;
	b/d = 0,01 bis 100;
	a/b = 0 bis 100, und
	das Verhältnis: d:(a + b) liegt in dem Bereich zwischen etwa 5:1 und etwa 1:50.

12. Carboxylatgruppen enthaltendes Polymer der Formel



worin M, a, b, d und p die gleichen Bedeutungen wie in Anspruch 11 haben.

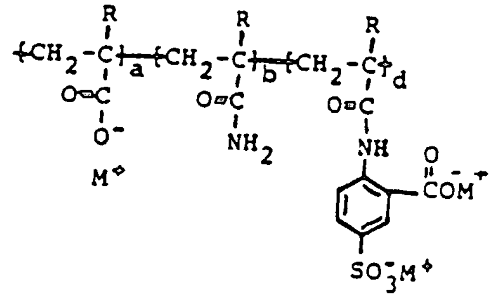
13. Carboxylatgruppen enthaltendes Polymer mit der Struktur



worin:

R	bei jedem Vorkommen einzeln ausgewählt wird aus Wasserstoff und Methylgruppen;
M	bei jedem Vorkommen einzeln ausgewählt wird aus Wasserstoff, Natrium, Kalium und Ammoniumionen und Mischungen davon;
R'	steht für eine multivalente brückenbildende Kohlenwasserstoff-Gruppe mit 1 bis 6 Kohlenstoffatomen, ausgewählt aus linearen Alkyl-, verzweigten Alkyl-, cyclischen und olefinischen Gruppen und Mischungen davon;
X	steht für $-SO_3M$, OH und Mischungen davon, und
a, b und d	stehen für ganze Zahlen, wobei deren Summe so groß ist, daß das Molekulargewicht des Carboxylatgruppen enthaltenden Polymers mindestens 2000 beträgt und die folgenden Beziehungen vorliegen: a/b = 0 bis 100, a/d = 0 bis 100, b/d = 0,01 bis 1000 und das Verhältnis d:(a + b) liegt zwischen etwa 10:1 und etwa 1:100, und
m	steht für 1 bis 6 und
n	steht für 1 bis 6, wobei die Summe m + n zwischen 1 und 8 liegt.

14. Carboxylatgruppen enthaltendes Polymer mit der Struktur

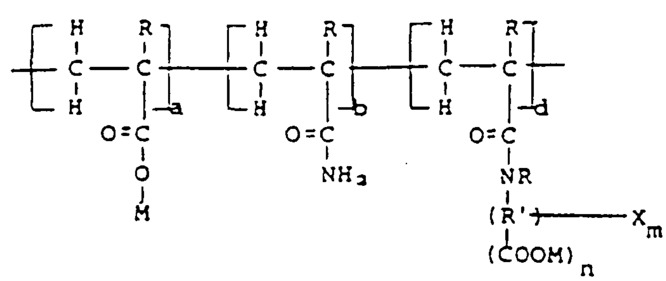


worin:

R	bei jedem Vorkommen einzeln ausgewählt wird aus Wasserstoff und Methylgruppen;
M	bei jedem Vorkommen einzeln ausgewählt wird aus Wasserstoff, Natrium, Kalium und Ammoniumionen und Mischungen davon; und
a, b und d	die gleichen Bedeutungen wie in Anspruch 13 haben.

Revendications

1. Un procédé pour synthétiser des polymères carboxylés solubles dans l'eau ayant des motifs monomères répétés de manière statistique, représentés par la formule :



dans laquelle

M est choisi parmi l'hydrogène, les groupes alkyles inférieurs en C_1-C_4, les métaux alcalins, les métaux alcalino-terreux, les sels d'amines primaires, secondaires ou tertiaires, les amines quaternaires et l'ion ammonium et leurs mélanges ;

R' est un groupe de pontage hydrocarboné multicovalent en C_1-C_{16}, choisi parmi les groupes alkyles à chaîne droite, les groupes alkyles à chaîne ramifiée, les groupes cycliques, aromatiques, hétérocycliques et oléfiniques et leurs mélanges (groupes fonctionnels) ;

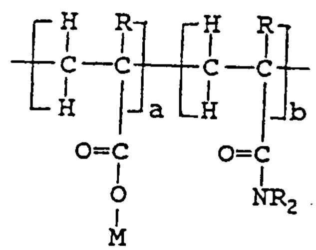
X est choisi parmi $-SO_3M$, $-PO_3M_2$, -COOR, -OR, -R'NR"$_2$, - R'N^+R_3Hal,

$$(OCH_2\overset{\displaystyle R}{\overset{|}{C}}H)_pOR$$

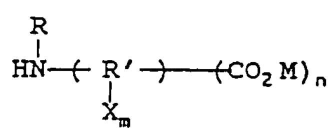
et leurs mélanges;
dans lesquels R" est

$$(CH_2\underset{\displaystyle R}{\underset{|}{C}}HO)_pR,$$

R et leurs mélanges et
R est choisi chaque fois indépendamment parmi H et les groupes alkyles inférieurs en C_1-C_4 ;
et dans laquelle
a, b et d sont des entiers satisfaisant les relations suivantes :
a,b est de 0 à 100,
b/d est de 0,01 à 100,
a/d est de 0 à 100
et la somme a+b+d est suffisante pour donner un poids moléculaire d'au moins 1000
et le rapport d/(a+b) est de 20:1 à 1:100 ; et dans laquelle
p est compris entre 1 et 16,
m est compris entre 0 et 16 et
n est compris entre 1 et 16, avec la condition que lorsque m est égal à 0, la somme m+n est de 1 à 20;
ledit procédé comprenant la réaction, dans un solvant courant, à une température d'au moins 100°C, de :
A. un polymère ayant un poids moléculaire d'au moins 500 et ayant des groupes fonctionnels amides pendants et représenté par la structure :



dans laquelle
R, M, a et b ont les mêmes significations que ci-dessus ; avec
B. un réactif chimique ayant la structure :



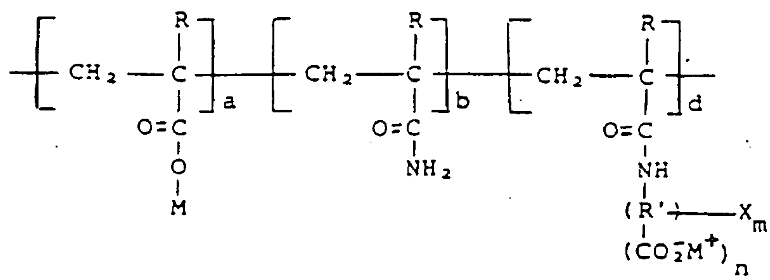
dans laquelle
R, R', M, X, m et n ont les significations ci-dessus ;
dans lequel le rapport molaire du réactif chimique aux groupes amines pendants dans le polymère est compris entre environ 5:1 et environ 1:100 ; et la réaction pendant une durée efficace pour effectuer une conversion d'au moins 2 moi % du réactif chimique en groupes pendants carboxylés sur le polymère ; et ensuite la récupération du polymère carboxylé soluble dans l'eau.

2. Le procédé selon la revendication 1, dans lequel
R est choisi individuellement chaque fois parmi l'hydrogène et les groupes méthyle et éthyle,
M est choisi individuellement chaque fois parmi l'hydrogène, le sodium, le potassium, les amines tertiaires, les ions ammonium quaternaires et les ions ammonium et leurs mélanges
R' est un groupe aliphatique à chaîne droite ou linéaire, cyclique ou aromatique en C_1-C_8 et leurs mélanges
X est $-SO_3M$, OH, $(OCH_2CH_2)_pOH$; et leurs mélanges,
p est de 1 à 12
m est de 0 à 4
n est de 1 a 4;
et le poids moléculaire du polymère carboxylé soluble dans l'eau est compris entre environ 2 000 et environ 20 000 000.

3. Le procédé selon la revendication 1 ou 2, dans lequel le solvant courant est choisi parmi l'eau, le diméthylformamide, le diméthylsulfoxyde, le diglyme et leurs mélanges.

4. Le procédé selon la revendication 1 ou 2, dans lequel le solvant courant est émulsifié dans l'eau en une phase huileuse continue de telle sorte que le polymère carboxylé soluble dans l'eau est récupéré sous forme d'une émulsion eau-dans-huile.

5. La synthèse des polymères carboxylés solubles dans l'eau représentés par la formule :



dans laquelle

R est choisi indépendamment dans chaque cas parmi l'hydrogène et les groupes alkyles en C_1-C_4,

M est choisi indépendamment chaque fois parmi l'hydrogène, les métaux alcalins, les sels d'amines tertiaires et les ions ammonium quaternaires et ions ammonium et leurs mélanges

R' est choisi parmi les groupes de pontage hydrocarbonés alkyles à chaîne droite, alkyles à chaîne ramifiée, alkaryles, aryles ou cycliques multi-covalents en C_1-C_8

X est choisi parmi $-SO_3H$, OH,

$$-\!\left(OCH_2\underset{\displaystyle R}{\underset{|}{C}}H\right)_{p}\!OR$$

et leurs mélanges ;

p est de 1 à 12,

m est de 0 à 6,

n est de 1 à 4;

a, b et d sont des entiers satisfaisant les relations suivantes :

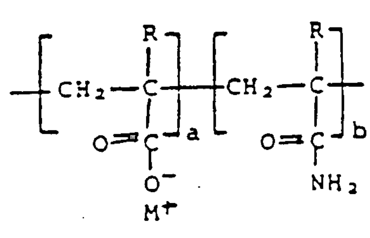
a/b est de 0 à 100,

a/d est de 0 à 100,

b/d est de 0,01 à 100

et le rapport d/(a + b) est compris entre environ 5:1 et environ 1:25 et dans laquelle la fréquence des a, b et d motifs monomères est aléatoire et la somme a + b + d donne un poids moléculaire d'au moins 1 000 ; ledit procédé comprenant la réaction, dans un solvant aqueux, de

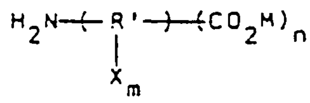
A. un polymère ayant des groupes fonctionnels amides pendants et représenté par la structure



dans laquelle

R, M, a et b ont les significations ci-dessus et dans laquelle la somme a+b donne un poids moléculaire d'au moins 500 ; et

B. un réactif ayant la structure



dans laquelle R', M, X, m et n ont les significations ci-dessus ; dans les conditions de réaction suivantes :

1. une température de réaction d'au moins 100 °C
2. une durée de réaction d'au moins 1/4 h
3. un rapport molaire du réactif chimique au polymère compris entre environ 2:1 et environ 1:50
4. une pression comprise entre la pression atmosphérique et 35 atmosphères ;

avec production et ensuite récupération desdits polymères carboxylés.

6. Un procédé selon la revendication 5, dans lequel

R est choisi individuellement dans chaque cas parmi l'hydrogène et le groupe méthyle,

M est choisi individuellement dans chaque cas parmi l'hydrogène, le sodium, le potassium, l'ammonium et leurs mélanges

R' est un groupe de pontage alkylène à chaîne droite ou ramifiée en C_2-C_6

X est $-SO_3M$,

$$-O-(CH_2CHO)_p-$$

R et leurs mélanges,

lorsque p est de 1 à 8;

a, b et d sont des entiers satisfaisant les relations suivantes :

a/b est de 0 à 50,

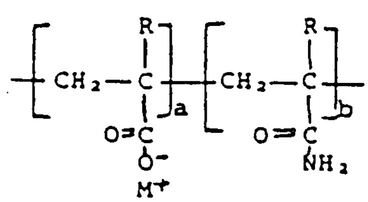
a/d est de 0 à 50,

b/d est de 0,01 à 10 et

d/(a+b) est compris entre 4:1 et 1:20,

et la somme a+b+d est telle que le polymère carboxylé a un poids moléculaire compris entre 2 000 et 20 000 000 et ledit procédé comprend la réaction à une température d'au moins 110 °C pendant au moins 1/2 h dans un solvant aqueux courant de

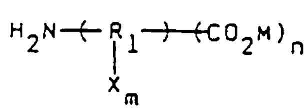
A. Un polymère ayant la structure



dans laquelle

R, M, a et b ont les significations ci-dessus et dans laquelle la somme a+b est telle que le poids moléculaire du polymère soit d'au moins 2 000; avec

B. un réactif chimique ayant la structure



dans laquelle

R_1, M et X sont définis ci-dessus et

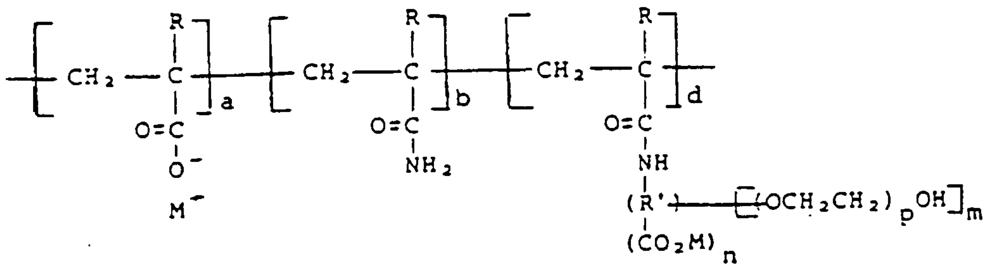
m est de 0 à 3

n est de 1 à 3 et la somme m+n est de 1 à 4 ; et

le rapport du réactif au polymère est compris entre environ 1:1 et environ 1:10 et la pression de réaction est d'au moins 1,25 atmosphères, et ensuite la récupération dudit polymère carboxylé.

7. Le procédé selon la revendication 5 ou 6, dans lequel le solvant aqueux est choisi parmi l'eau et une émulsion eau-dans-huile.

8. Un procédé pour synthétiser un polymère carboxylé représenté par la formule



dans laquelle

R est choisi individuellement chaque fois parmi l'hydrogène, le groupe méthyle et le groupe éthyle

M est choisi individuellement chaque fois parmi l'hydrogène, le sodium, le potassium, les sels d'amines tertiaires et les ions ammonium et leurs mélanges

R' est un groupe de pontage alkylène à chaîne droite ou linéaire en C_1-C_6;

p est de 1 à 12,

m est de 1 à 6,

n est de 1 à 6,

et la somme n+m est de 1 à 10;

a, b et d sont des entiers satisfaisant les relations :

a/d est de 0 à 50,

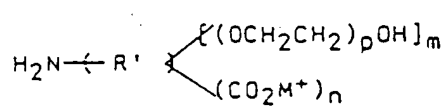
a/b est de 0 à 50,

b/d est de 0,1 à 20,

d/(a+b) est de 5:1 à 1:10 et

la somme a+b+d est suffisante pour donner un poids moléculaire d'au moins 2 000 ; ledit procédé comprenant la réaction dans un solvant aqueux, à un pH d'environ 3-8, pendant au moins 1/4 h à une température d'au moins 110 °C, dans un réacteur à pression contrôlée, des ingrédients :

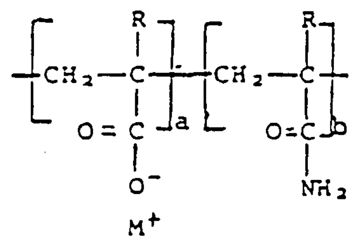
A. un réactif chimique :



dans lequel

R', M, p, m et n ont les significations ci-dessus ; et

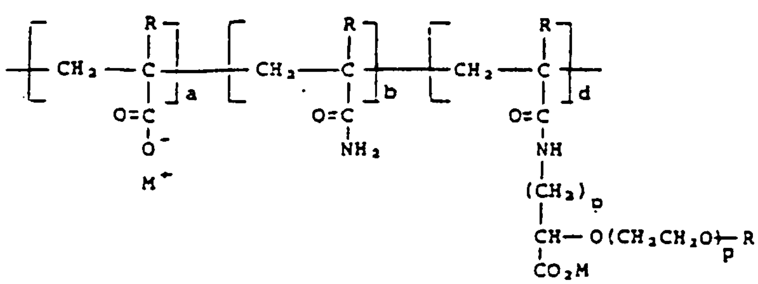
B. un polymère vinylique soluble dans l'eau ayant des groupes amides pendants représenté par :



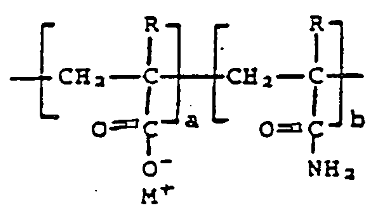
dans laquelle

R, M, a et b ont les significations ci-dessus ; et dans lequel le rapport molaire du réactif aux groupes amides pendants sur le polymère est compris entre environ 1:1 et environ 1:5 ; et ensuite la récupération du polymère carboxylé.

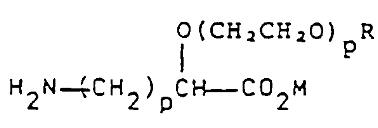
9. Le polymère carboxylé



qui est synthétisé, dans un réacteur à pression contrôlée, par réaction d'un polymère précurseur



avec un réactif :



dans un solvant de réaction aqueux à une température d'au moins 100 °C pendant au moins 1/4 h avec un rapport molaire du polymère précurseur au réactif compris entre environ 20:1 et environ 1:2, et dans lequel

R est choisi individuellement à chaque fois parmi l'hydrogène et le groupe méthyle ;

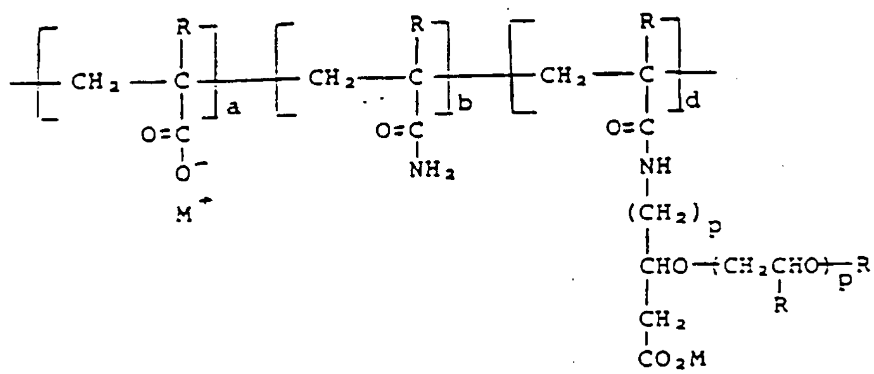
M est choisi individuellement à chaque fois parmi l'hydrogène, les métaux alcalins, les amines tertiaires et les ions ammonium et leurs mélanges

p est compris chaque fois entre 0 et 12 ;

a, b et d sont des entiers satisfaisant les relations :
a/d est de 0 à 100,
a/b est de 0 à 100,
b/d est de 0,01 à 100 et
d/(a + b) est compris entre environ 10:1 et environ 1:100 et dans lequel
la somme a + b + d est telle que le polymère carboxylé a un poids moléculaire d'au moins 1 000.

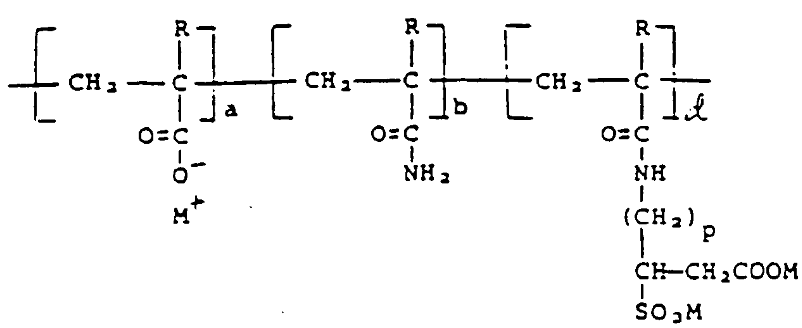
10. Le polymère carboxylé selon la revendication 9, qui est synthétisé dans un solvant de réaction aqueux à une température d'au moins 120 °C pendant au moins 1 h avec un rapport molaire du polymère précurseur au réactif de 10:1 à 1:1 et dans lequel :
R est un atome d'hydrogène
M est choisi parmi l'hydrogène, le sodium, le potassium et les ions ammonium et leurs mélanges
et le polymère a un poids moléculaire compris entre environ 2 000 et environ 20 000 000.

11. Le polymère carboxylé représenté par la structure



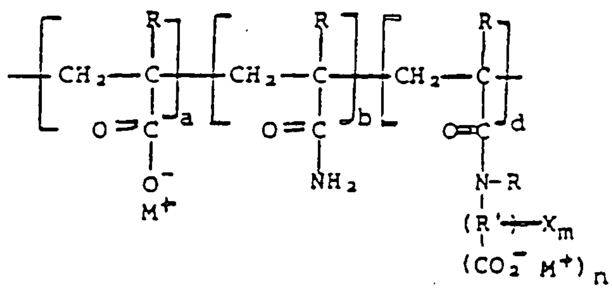
dans laquelle
M est choisi individuellement chaque fois parmi l'hydrogène, le sodium, le potassium, les ions ammoniums et leurs mélanges ;
a, b et d sont des entiers tels que :
la somme a + b + d est suffisante pour donner un poids moléculaire d'au moins 1 000 ;
p, dans chaque cas, est de 0 à 6;
a/d est de 0 à100;
b/d est de 0,01 à 100;
a/b est de 0 à 100 et
le rapport d(a + b) est compris entre environ 5:1 et 1:50.

12. Le polymère carboxylé représenté par la formule



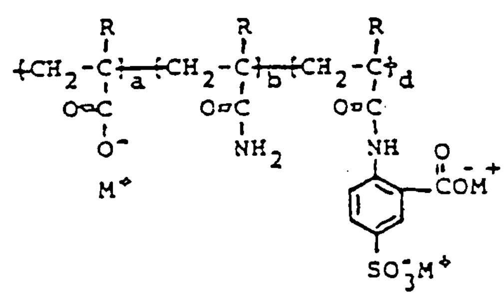
dans laquelle M, a, b, d et p ont les significations indiquées dans la revendication 11.

13. Le polymère carboxylé est représenté par la structure



dans laquelle
R est choisi individuellement dans chaque cas parmi l'hydrogène et le groupe méthyle ;
M est choisi individuellement dans chaque cas parmi l'hydrogène, le sodium, le potassium et les ions ammoniums et leurs mélanges ;
R' est un groupe de pontage hydrocarboné multivalent en C_1-C_6 choisi parmi les groupes alkyles à chaîne droite et à chaîne ramifiée et cycliques et les groupes oléfiniques et leurs mélanges ;
X est choisi parmi -SO_3M, OH et leurs mélanges et
dans laquelle a, b et d sont des entiers dont la somme est telle que le poids moléculaire du polymère carboxylé est d'au moins 2 000 et dans laquelle on a les relations suivantes :
a/b est de 0 à 100,
a/d est de 0 à 100,
b/d est de 0,01 à 1000 et
le rapport d/(a+b) est compris entre environ 10:1 et environ 1:100 et dans laquelle
m est un nombre de 1 à 6,
n est un nombre de 1 à 6 et la somme m+n est un nombre de 1 à 8.

14. Le polymère carboxylé représenté par la structure :



dans laquelle R est choisi individuellement chaque fois parmi l'hydrogène et le groupe méthyle;
R est choisi individuellement chaque fois parmi l'hydrogène, le sodium, le potassium et les ions ammonium et leurs mélanges, et
a, b et d sont les mêmes qu'à la revendication 13.